THE CRYSTAL AND MOLECULAR STRUCTURES OF

TRI-(*p*-FLUOROPHENYL)-AMINE AND

TRI-(*p*-IODOPHENYL)-AMINE

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DISSERTATION

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By

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TABLE OF CONTENTS

        Tri-(p-fluorophenyl)-amine
        Tri-(p-iodophenyl)-amine

        Tri-(p-fluorophenyl)-amine
        Tri-(p-iodophenyl)-amine

        Thermal Motion
        Molecular and Crystal Structures

LIST OF TABLES

Table   Page

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Although the valence geometry of trivalent nitrogen is recognized as a classic problem in organic chemistry, the literature contains little reliable information concerning the geometry of triarylamines. A preliminary investigation by Schlemper and Hausmann (30) revealed the space group and cell dimensions of the four tri-(p-halophenyl)-amines, but no structure analyses of these compounds have been reported. Crystals of triphenylamine itself do not appear to be suitable for X-ray analysis (17). An electron-diffraction study of triphenylamine has been reported (28), but it does not provide a completely satisfactory answer to the question of geometry of the nitrogen valences. Because of the need for data on the geometry of nitrogen in arylamines, the determination of the crystal and molecular structures of tri-(p-fluorophenyl)-amine (TFPA) and tri-(p-iodophenyl)-amine (TIPA) was undertaken as the subject of this dissertation.

The geometry of the valence bonds about the nitrogen atom in molecules such as NR_3 and about the phosphorus and arsenic atoms in the homologues PR_3 and AsR_3, where R = H-, CH_3-, phenyl-, p-tolyl-, and so forth, is of great theoretical interest. Bond distances and angles for some of these compounds are listed in Table I. Notable is the

TABLE I

BOND LENGTHS AND ANGLES OF SOME TRISUBSTITUTED
AMINES, PHOSPHINES, AND ARSINES

	$\angle$R-N-R($^\circ$)	R-N($\overset{\circ}{A}$)	$\angle$R-P-R($^\circ$)	R-P($\overset{\circ}{A}$)	$\angle$R-As-R($^\circ$)	R-As($\overset{\circ}{A}$)
H	106.8	1.014	93.8	1.421	91.8	1.519
CH_3	108.7	1.472	99.1	1.841	96.0	1.959
Phenyl	116.0	1.42	102.99	1.828	. . .	. . .
p-Tolyl	. . .	. . .	. . .	. . .	102.0	1.96

decrease in valence angles when passing from NH_3 (16, 21, 26, 27) to PH_3 (21, 26, 27) to AsH_3 (9, 26, 27). These angles would all be 90° if pure p-electron valences were the only valences involved. Mulliken (27) suggests the observed angles can best be understood in terms of the stabilization energy obtained in s-p hybridization in equilibrium with the nonbonded repulsion energy between H atoms in the NH_3 molecule and s-p, s-d, and $p\pi$-$d\pi$ hybridization coupled with nonbonded repulsions between H atoms in the molecules PH_3 and AsH_3. Specifically, he attributes the decrease in valence angle when passing from NH_3 to PH_3 to AsH_3 to the $p\pi$-$d\pi$ hybridization which can occur only for arsenic and phosphorus and to the decrease in H-H nonbonded repulsions related to the considerably larger sizes of arsenic and phosphorus atoms as compared with the nitrogen atom. However, Mellish and Linnett (26) conclude that the

decrease in valence angle results from changes in hybrid-

ization related to the decreasing electronegativity of the

central atom.

Microwave studies of trimethylamine (25), trimethyl-

phosphine (24), and trimethylarsine (23) have shown that

these molecules have larger valence angles about the central

atoms than do their corresponding hydrogen analogues,

ammonia, phosphine, and arsine. (See Table I.)

Attempts to determine the crystal structure of tri-

phenylamine by X-ray analysis were terminated (17) because

the crystals examined were nearly always twinned and the

number of molecules per asymmetric unit is four. However,

the molecular structure in the gaseous state has been

determined by Sasaki and co-workers (28) by means of

electron diffraction. The C-N-C angle* found was $116(2)^{\circ}$

and the C-N bond lengths* were $1.42(04)$ $\overset{o}{A}$. The twist angle

ϕ of the phenyl groups is equal to $47(5)^{\circ}$, ϕ being defined

as the angle of twist of a phenyl group about its C-N axis

from the position in which the threefold symmetry axis lies

in the plane of the phenyl group. The authors believe that

nonbonded H-H repulsions are at a minimum at this twist

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*Here and elsewhere in this dissertation the estimated
standard error of a structural parameter, such as an angle
or a bond length, is specified by a number in parentheses
following the parameter value. The digits of this number
correspond to the least-significant digits of the parameter.
Similarly, when an average value of a parameter is given,
the root-mean-square deviation from the average usually
follows it in square brackets.

angle. They point out that the C-N distance in triphenyl-amine (1.42 $\overset{o}{A}$) is shorter than the corresponding distance in trimethylamine (1.472 $\overset{o}{A}$). To them this would suggest the contribution of numerous resonance forms, such as I,

$$(C_6H_5)_2N^+=\left\langle\overline{\underline{\bigcirc}}\right\rangle:^-$$

I
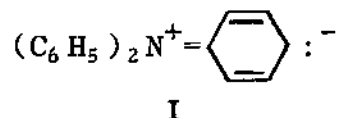
which involved delocalization of the unshared electron pair of the nitrogen atom. According to the arguments of Dewar (14), the shortening is probably more properly to be attributed to the increased s character in the carbon bonding orbital and perhaps to some similar increase in s character of the nitrogen bonding orbital.

Although Sasaki and co-workers seemed to prefer the pyramidal description, they specifically admitted the possibility that the actual equilibrium valence configuration is plane trigonal and that it only appears pyramidal because of thermal bending motion. Thus, the electron-diffraction study does not exclude the possibility of a plane valence configuration at nitrogen, though it clearly does limit the possible configurations to those which are nearer the plane configuration than to the tetrahedral one.

It is a point of some interest that if resonance forms such as I are indeed important contributors then the configuration at the nitrogen atom may be expected to depend on the nature of any substituent groups that might be attached to the rings. For example, the substitution of

NO_2 groups in the three _para_ positions should enhance the importance of the three equivalent forms represented by I and might thereby tend to make the central nitrogen atom come closer to the plane configuration. Other substitutions, by halogen atoms for example, might have varying inductive effects depending on the electronegative character of the substituent atoms.

Attempts at elucidating the structure of triphenylamine have also been made through dipole-moment and spectroscopic studies. From dipole-moment studies, taking the dipole moment of triphenylamine to be 0.55 Debye units, Leonard and Sutton (22) have calculated the central angle C-N-C to be 114°. However, there is an inherent difficulty in establishing accurately the value of such a small moment, namely, the difficulty of estimating correctly the magnitude of the atomic polarization which enters into the calculation of the moment. Other values for the moment ranging from zero to 0.71 Debye units have been reported in the literature (8, 29). The results of the dipole-moment studies cannot, therefore, be considered definitive.

Similarly, neither ultraviolet (18) nor infrared spectra (19) have yielded much information on the valence geometry of nitrogen in triphenylamine. The ultraviolet spectra do suggest some double-bond character in the N-C bonds; the infrared spectra suggest, but hardly prove, the plane trigonal geomtry, or something close to it.

A compound of related interest whose structure has been reported (33) is the 2,2-diphenyl-1-picrylhydrazyl free radical shown in Figure 1. Atoms N_{19}, N_{20}, C_7, and
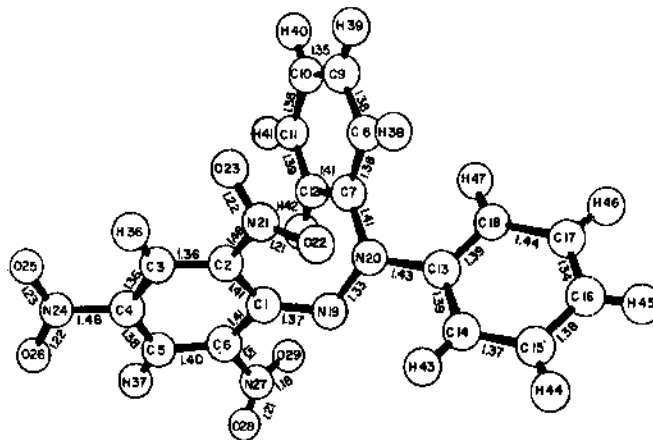
Fig. 1--The 2,2-diphenyl-1-picrylhydrazyl free radical.

C_{13} are reported to lie in a plane. The plane of the picryl moiety is twisted approximately 63° from the plane of N_{19}, N_{20}, C_7, and C_{13}. Because of this twist the stabilization expected from conjugation would be reduced. The planes of benzene rings C_7-C_{12} and C_{13}-C_{18} are twisted by 48° and 22°, respectively. The latter ring would be expected to have more π orbital overlap with the nitrogen atom because of its smaller twist angle. The geometry around each nitrogen atom is consistent with sp^2 hybridization. The N_{19}-N_{20} bond length (1.33 $\overset{O}{A}$) is intermediate between that expected for a single bond (1.45 $\overset{O}{A}$) and a double bond (1.23 $\overset{O}{A}$).

The planarity of the nitrogen valences in the hydrazyl might suggest the likelihood of planarity at nitrogen in triphenylamine. However, the presence of the unpaired electron on the free radical molecule means that the structural analogy between the radical and the amine is only a rough one at best. An important resonance contribution (involving no charge separation) of a form having a double bond between N_{19} and N_{20} and the free electron on N_{19} would be reasonable; and it would be consistent with the plane configurations found for N_{20}. No analogous form can be written for triphenylamine.

Daly has reported (12) an X-ray analysis of the crystal structure of triphenylphosphine which shows that the molecule has the "expected" pyramidal configuration about the nitrogen atom. The average C-P-C angle is $103.0[0.6]^{\circ}$ and the average P-C bond length is $1.828[4]$ $\overset{\circ}{A}$. One of the phenyl rings (called B) has a twist about 30° different from the other two. "This distortion," Daly states, "cannot be due to intramolecular repulsions of the CH groups as twisting the B-ring to the symmetrical position would only reproduce contacts already present." He concludes that intermolecular repulsions may be the cause of the distortion, although the shortest of the nonbonded repulsions does not involve the distorted ring. However, it was also pointed out that two of the shortest nonbonded C-C intramolecular distances involve the distorted ring and are

shorter than the shortest nonbonded intermolecular distance by approximately 0.38 $\overset{o}{A}$. The average P-C bond length found in triphenylphosphine is shorter than the corresponding one in trimethylphosphine, 1.841(3) $\overset{o}{A}$, indicating according to Daly only a slight degree of conjugation in the phenyl derivative.

Preliminary X-ray studies (32) have revealed the space group and cell parameters of triphenylarsine, but no further work has been reported.

Trotter (31) has reported the crystal structure of tri-p-tolylarsine. The C-As-C angles and As-C bonds are reported to be $102.0(2.0)^{o}$ and 1.96(05) $\overset{o}{A}$, respectively. Since the space group is $R\overline{3}$ and there are two molecules per unit cell, each molecule is required to have symmetry C_3. Trotter suggested that the "ideal" model for the molecule in the absence of any intramolecular steric interference would be one in which the normals to the aromatic rings lie in the planes defined by the lone electron pair and the As-C bonds. This configuration would allow maximum π overlap between the lone pair and the benzenoid rings. However, this ideal model does exhibit steric hindrance between ortho carbon atoms and between their respective hydrogen atoms. Each ring in the true structure is twisted about its As-C bond by 36° in order to relieve this stress. The intermolecular distances correspond to normal van der Waals interactions.

Andersen has investigated several compounds of related and interesting stereochemistry. Two compounds, triphenylmethane (3) and triphenylmethyl free radical (2), were investigated by electron diffraction and another two, tri-p-nitrophenylmethyl free radical (5) and tri-p-methoxyphenylmethyl carbonium ion (4), were investigated by X-ray crystal analyses. The investigation of triphenylmethane revealed a C-C-C angle, called γ, at the central carbon atom of $112(2)^{\circ}$ and a C-C distance from the central atom of $1.53(02)$ $\overset{\circ}{A}$. The ring twist angle ϕ' is $45(5)^{\circ}$, the zero of ϕ' specifying the configuration with the ring plane normal in the plane defined by the threefold axis and the central bond to the ring.

The investigation of triphenylmethyl established γ as $116-118^{\circ}$ and the central C-C bond length as 1.48 $\overset{\circ}{A}$. Anderson suggests that the deviation of γ from the 120° equilibrium value expected for sp^2 hybridization of the central carbon atom probably results from the large thermal motion in the molecule (1). The twist angle is reported as $40-45^{\circ}$; it appears to be dependent upon intramolecular C-C repulsions rather than upon intramolecular repulsions between ortho hydrogens of adjacent rings.

The crystal structure of tri-p-nitrophenylmethyl as reported by Andersen (5) revealed central bond angles not differing significantly from 120° and an average central C-C bond length of 1.47 $\overset{\circ}{A}$. The results are in agreement

with the space-group requirement that the molecule have twofold symmetry and, therefore, a planar arrangement of the central bonds. One phenyl group has a twist of 40°, and the other two exhibit twists of 30°. The 30° twist of the two phenyl groups is attributed to _ortho_ hydrogen contacts and the larger twist of the third ring to packing.

In the tri-_p_-methoxyphenylmethyl carbonium ion (4) the three central valence bonds lie in the same plane, or nearly so, and the phenyl group has a twist of approximately 30°. In this case the ion has exact symmetry C_3.

The crystal structure of triphenylmethyl perchlorate (15) has been determined by Gomes de Mesquita and co-workers. The triphenylmethyl carbonium ion has exact symmetry D_3. The three central bonds are coplanar with a bond length of 1.454 $\overset{O}{A}$, and the twist angle ϕ' is $31.8(6)^O$. The twist results from intramolecular H-H contacts.

Lip Lin Koh has determined the crystal structure of tri-(_p_-aminophenyl)carbonium perchlorate (20). The configuration about the central carbon atom is planar, the average central C-C bond length being 1.446 $\overset{O}{A}$, with the three benzene rings exhibiting twists ϕ' from the plane of 34°, 34°, and 27°. The twist angles are apparently determined by adjacent _ortho-ortho_ C-C, C-H, and H-H nonbonding distances and by the packing of the molecules.

The structural data on the triarylmethyl radicals and triarylcarbonium ions studied establish that for both the

radicals and the ions the characteristic geometry for the central carbon atom is plane trigonal. However, as in the case of 2,2-diphenyl-1-picrylhydrazyl, the analogy between these species and triphenylamine is imperfect. For either a triarylmethyl radical or the corresponding carbonium ion it is possible to write reasonable resonance structures which are analogous to I but which do not involve charge separation. Such structures would be more important contributors than I is for triphenylamine.

A class of compounds of further stereochemical interest is that of the carbanions. Andersen and co-workers (6, 7) have reported the crystal structure of sodium and potassium tricyanomethides, $NaC(CN)_3$, and $KC(CN)_3$. The anions were found to be essentially planar. Sass and co-workers (10, 11, 13), after investigating the crystal structures of pyridinium dicyanomethylide, $C_5H_5N^+-C^-(CN)_2$, and ammonium tricyanomethide, $NH_4C(CN)_3$, have concluded that there are significant deviations from planarity. In the former compound the carbon and nitrogen atoms of the two cyano groups deviate from the least-squares best plane of the anion by 0.08 and 0.13 $\overset{o}{A}$, respectively. The central carbon atom of the tricyanomethide anion was found to be 0.13 $\overset{o}{A}$ above the plane described by the three nitrogen atoms of this anion. Sass and co-workers conclude that these deviations from planarity imply that the central carbon atom may possess a significant amount of negative charge.

However, Andersen and co-workers suggest that the deviations from planarity of the anions in the sodium, potassium, and ammonium compounds are packing effects rather than consequences of a significant negative charge held by the central carbon atom. The deviations found in the pyridinium dicyanomethylide are probably caused by packing or by contacts between _ortho_ hydrogen atoms and carbon atoms of the CN groups.

No structural data are available for carbanions more closely resembling triphenylamine. The analogy would in any case be imperfect for reasons similar to those already given for the triarylmethyl radicals and carbonium ions.

In summary, one can say that at the beginning of the work reported here the available structural data, on triphenylamine itself and on analogous compounds, were not sufficient to resolve the question of whether the nitrogen valences in triphenylamine are in a flattened pyramidal configuration or whether they are in a plane configuration.

Crystals of the four tri-(p-halophenyl)-amines were available for X-ray structure analysis. The fluoro- and iodo- derivatives were chosen for study in order to determine the effects, if any, of substituents with significantly differing electronegativities upon the valence geometry. From the unit-cell parameters of Schlemper and Hausmann (30) it is almost certain that the fluoro-, chloro-, and bromo- derivatives are isostructural to the

degree that a solution of the phase problem for the fluoro-
compound is a solution for the chloro- and bromo- compounds
as well.

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CHAPTER II

EXPERIMENTAL

Tri-(p-fluorophenyl)-amine

Colorless prismatic crystals of tri-(p-fluorophenyl)-amine (TFPA) were obtained from Robert I. Walter of the University of Illinois, Chicago, for this study. A suitable specimen was mounted on a thin glass fiber so that the spindle axis coincided approximately with the long prism axis (later designated as the c axis). This crystal, which had dimensions of approximately 0.32 x 0.35 x 0.47 mm., was used for the determination of cell parameters and for collection of intensity data. The diffraction symmetry displayed in precession photographs was monoclinic. The observed systematic absences of reflections,

$$h0\ell \text{ absent when } \ell \text{ is odd,}$$

$$0k0 \text{ absent when k is odd,}$$

uniquely specify the centric space group $P2_1/c$ (4). The approximate cell parameters obtained from precession photographs were found to agree with those previously reported (10), except for the angle β, which was found to be 108.5° rather than 104.6° as reported.

The crystal was transferred to the Oak Ridge computer-controlled X-ray diffractometer (1). The instrumental angles two-theta (2θ), omega (ω), chi (X), and phi (ϕ)

necessary to maximize the reflected intensity while center-
ing the reflection in the counter were individually deter-
mined for twelve reflections at about $23^{\circ}C$, using Cu $K\alpha_1$
radiation ($\lambda = 1.54051 \overset{\circ}{A}$). The angle data were used as
observations in a least-squares process in which three
orientation parameters and the cell constants were refined.
The refined cell parameters for TFPA are:

$$a = 10.4360(3) \overset{\circ}{A}$$
$$b = 17.3788(6) \overset{\circ}{A}$$
$$c = 8.4872(2) \overset{\circ}{A}$$
$$\cos \beta = -0.31813(4) \ (\text{or} \ \beta = 108.55^{\circ})$$

The density from a flotation measurement (10) in aqueous
potassium iodide is 1.35 g cm^{-3}, fixing the number of mole-
cules per cell at four, since for four molecules of formula
weight 299.284 g $mole^{-1}$ per unit cell volume of 1459.316 $\overset{\circ}{A}{}^3$
the calculated density is 1.362 g cm^{-3}.

The crystal dimensions and the orientations of the
crystal faces were measured utilizing the chi and phi
motions of the diffractometer and a microscope with a
measuring eyepiece. The data obtained were used later for
making absorption measurements.

The data, to the limit $(\sin\theta)/\lambda = 0.64$, were recorded*
using Cu $K\alpha$ radiation by the computer-controlled diffrac-
tometer using the theta, two-theta (θ-2θ) step-scan

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*The data had already been collected by George M.
Brown but had not even been preliminarily processed.

technique for the two-theta range of 30-159.6^O and the omega (ω) step-scan technique (8) for the two theta range of 1-40°. The X-ray tube was operated at thirty-five kilovolts constant potential and twenty milliamperes current.

The two-theta scans were recorded under the following conditions: (a) the step width was 0.05^O in 2θ; (b) the total width of scan for each reflection was two degrees plus the width of the α_1-α_2 doublet separation; (c) the count time for each point in a scan was two seconds and the time for background counts taken at the beginning and end of each scan was ten seconds; (d) a nickel filter was used for reflections within the 2θ range 30-90° in order to eliminate the Cu K$_\beta$ radiation; (e) no β-filter was used for reflections recorded above 90° in 2θ; and (f) the takeoff angle at the X-ray tube was three degrees.

The bisecting configuration of the chi circle ($\omega = 0^O$) was used for the 2θ range up to 134.4^O and the parallel configuration ($X = 90^O$) for the 2θ range between 134.4^O and 159.1^O. The reason for switching to the parallel mode was to collect data in the angle range above 134.4^O, a region which would otherwise be inaccessible because of the physical limitations of the chi circle--that is, the chi circle would be driven to a collision with some other component of the diffractometer. Reference reflections, 400 for the bisecting configurations and 4,$\overline{16}$,2 for the parallel configuration, were recorded after every twenty reflections as a check on the stability of the instrument and crystal.

In the omega step-scan technique three scans were run
for each reflection. The first scan was run with the
counter arm set at the computed 2θ value of the reflection;
the next two scans were run with the arm offset first lower
and then higher in 2θ just enough to determine background.
The net count of the reflection was taken as the integrated
count of the first scan minus the average of the integrated
counts of the two background scans. This procedure, with
proper choice of takeoff angle, counter aperture, and 2θ
offset, provides more reliable background determinations for
the low-angle reflections than does the θ-2θ technique, in
which the effect of the absorption edge of the filter just
below the peaks for α-radiation makes proper background
measurements impossible on the low-angle sides of the peaks.

The width of each ω scan was one degree, the step
width was 0.025°, and the count time for each point in a
peak scan or background scan was two seconds. No filter
was used for ω step-scans. The takeoff angle at the X-ray
tube was set at 0.8°; and the counter slit and the counter
offset $\Delta(2\theta)$ were set so that the three scans for each
reflection would not overlap, and so that the slit width
and $\Delta(2\theta)$ (both the same) were always less than the 2θ
separation between the α peak and the β peak, but the slit
width was always wide enough to admit the α doublet.

The net count (sum of counts over a scan minus the
corresponding background correction) of a reflection is the

observed intensity I_O of the reflection; it is proportional to the so-called integrated intensity and to the integrated reflection (6). The proportionality constant k is determined by the crystal size, the intensity of the incident beam, the counter efficiency, and the conditions of the scan; in practice, however, the constant is not easily determined directly from experiment. Therefore, the intensities and the observed structure factors related to them are usually not on the proper absolute scale at the beginning of structure analysis.

The raw data in the form of the intensities I_O and the corresponding statistical standard errors $\sigma_s(I_O)$ were punched on paper tape automatically by the diffractometer. The reference intensities were used to normalize each reflection intensity to a fixed standard value of intensity of the appropriate reference reflection. The slight variations of the reference intensities were assumed to represent slowly varying instrumental conditions. A linear relation of incident X-ray intensity to time was assumed to hold between each pair of adjacent reference intensities. Reflection data sets normalized to the two different reference reflections (400 and $4,\overline{16},2$) were scaled to each other through an experimental correlation of the two reference intensities.

After the preliminary normalizing and scaling, the observed structure-factor squares F_O^2 and the corresponding

statistical standard errors $\sigma_s(F_o^2)$ were computed by the equations (6)

$$F_o^2 = \frac{KI_o}{TLp} \, ,$$

$$\sigma_s(F_o^2) = \frac{K\sigma_s(I_o)}{TLp} \, .$$

In these equations L is the Lorentz factor, which for the diffractometer method used is $1/\sin2\theta$; p is the polarization factor $(1 + \cos^2 2\theta)/2$, appropriate for unpolarized incident radiation; T is an absorption factor (see below); and K is a constant which includes a factor involving only universal constants and the proportionality factor k relating the intensities I_o to the integrated reflections.

The absorption factors were calculated[*] by the method of Busing and Levy (2). The linear absorption coefficient μ is computed as

$$\mu = \rho \sum_i^N w_i (\mu/\rho) \, ,$$

where ρ is the crystal density, $(\mu/\rho)_i$ is the mass absorption coefficient and w_i is the weight fraction for the element i in the molecule. The values of $(\mu/\rho)_i$ were taken from the International Tables for X-ray Crystallography (5). The calculated value of μ for TFPA is 9.28 cm^{-1}. The transmission factor T is computed by the equation

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[*]The computer programs used in the analysis of the crystal and molecular structures of TFPA and TIPA are listed in the Appendix.

$$T = \int (1/v) \exp[-\mu(r_\alpha + r_\beta)] \, dv,$$

where

v = crystal volume,

μ = linear absorption coefficient,

r_α = path length along primary beam direction,

r_β = path length along diffracted beam direction.

The calculated correction factors for absorption (values of T^{-1}) ranged from 1.08 to 1.40. The first derivatives of the transmission factors with respect to μ were also computed for subsequent use in extinction corrections.

Since the factor K was not yet known, the values of F_o^2 and $\sigma_s(F_o^2)$ were calculated with K set to unity. The data for replicate observations and for equivalent observations were averaged to produce a set of 3020 independent observations of F_o^2 with corresponding standard errors $\sigma_s(F_o^2)$. These data and standard errors were punched on cards for subsequent use in the structure analysis. On each reflection card the quantity $(dT/d\mu)/T$ was also punched. Individual scale-factor identifiers (numeric labels) were assigned to groups of reflections in several ranges of 2θ. as follows: $1-40^O$ (ω step-scans, unfiltered radiation); $30-90^O$ (2θ step-scans, filtered radiation); $90-134.4^O$ (2θ step-scans, unfiltered radiation); $134.4-159.4^O$ (2θ step-scans, unfiltered radiation, parallel mode). The purpose of these scale-factor identifiers was to facilitate adjustment of the scale factors individually in the subsequent least-squares refinement.

The statistical method of Wilson (11) was used to
obtain an approximate value for the scale factor K (see
above) needed to bring the punched values of F_o^2 and $\sigma_s(F_o^2)$
to absolute scale. The Wilson method also provided the
value 5.08 $\overset{o}{A}^2$ for the parameter B of the Debye-Waller iso-
tropic temperature factor, $\exp[-B(\sin\theta)^2/\lambda^2]$. This temper-
ature factor takes account of the smearing of atomic
electron densities caused by thermal vibrations; it is a
multiplication factor to be applied in structure-factor
calculations to the atomic scattering factors, which are
tabulated for atoms at rest.

The normalized structure factors, E's, were also
computed according to the equation (3)

$$E = \frac{K^{1/2}F_o}{\epsilon\left[\sum_{j=1}^{N} f_j^2\right]^{1/2}\exp[-B(\sin\theta)^2/\lambda^2]}$$

In this equation, F_o is the unscaled observed structure-
factor magnitude, K is the scale factor, f_j is the scatter-
ing factor for atom j at rest, and N is the total number of
atoms in the unit cell. The factor ϵ is a statistical
factor determined by the symmetry; it allows for the fact
that reflections of particular lines or planes in reciprocal
space have average intensities which are integral multiples
of the average of the general reflections (9). For space
group $P2_1/a$, $\epsilon = 2$ for the $h0\ell$ and $0k0$ reflections and $\epsilon = 1$
for all other reflections. The distribution of the

magnitudes of normalized structure factors is dependent on whether or not the space group is centrosymmetric. By examining the distribution of E values one can predict with reasonable certainty the presence or absence of a center of symmetry. The experimental distribution of E values is compared in Table II with the theoretical distributions for random centric and acentric distributions of atoms in the unit cell (7). The comparison clearly confirms the assignment to space group $P2_1/a$ from the systematic absences.

TABLE II

EXPERIMENTAL DISTRIBUTION OF E VALUES FOR TFPA
COMPARED WITH THE THEORETICAL CENTRIC
AND ACENTRIC DISTRIBUTIONS

	Experimental	Theoretical (Centric)	Theoretical (Acentric)
Average magnitude of E	0.773	0.798	0.886
Average magnitude of E^2	1.000	1.000	1.000
Average magnitude of (E^2-1)	1.034	0.968	0.736
Percentage of E values greater than 1.00	28.03	32.00	37.00
Percentage of E values greater than 2.00	4.69	5.00	1.80
Percentage of E values greater than 3.00	0.86	0.30	0.01

Tri-(p-iodophenyl)-amine

Crystals of tri-(p-iodophenyl)-amine (TIPA) were obtained from Robert I. Walter. The crystals, colorless prisms, were examined with the aid of a polarizing microscope; a suitable specimen was mounted on a thin glass fiber such that the spindle axis coincided with the long prism axis (later identified as the c axis in the hexagonal description of the cell). The crystal had dimensions of approximately 0.30 x 0.27 x 0.23 mm. From a series of precession photographs the approximate cell dimensions and the symmetry reported by Schlemper and Hausmann (10) were verified. The Laue symmetry and the lack of systematic absences indicated two possible rhombohedral space groups, R3 and R$\bar{3}$, but allowed no choice between them. For convenience in computation and visualization of the structure, the alternate hexagonal description of the rhombohedral lattice was employed (4).

The crystal was transferred to the Oak Ridge computer-controlled X-ray diffractometer. In the same manner as in the study of TFPA, angle settings from twelve reflections of TIPA recorded at approximately 24.8°C with Mo K$_{\alpha_1}$ radiation (λ = 0.70926 Å) were used as input to a least-squares calculation in which three orientation parameters and the cell constants were refined. The refined hexagonal cell parameters for TIPA are:

$$a = b = 44.371(9) \text{ Å},$$
$$c = 10.131(17) \text{ Å}.$$

The density from a flotation measurement (10) in a solution of bromoform and cyclohexane is 2.14 g cm^{-3}. The volume of the unit cell based upon the refined cell parameters is 17272.9 $\overset{O}{A}^3$. For thirty-six molecules of TIPA per hexagonal cell, each molecule having a formula weight of 623.013 g mole^{-1}, the calculated density is 2.16 g cm^{-3}.

The crystal dimensions and the orientations of the crystal faces were measured by the same procedure followed for TFPA in order that absorption and extinction corrections could be made.

Intensity data for 4956 independent reflections, to the limit $(\sin\theta)/\lambda = 0.64$, were recorded with the Oak Ridge computer-controlled diffractometer using Mo K$_\alpha$ radiation. The X-ray tube was operated at fifty kilovolts constant potential and fourteen milliamperes current.

The θ-2θ step-scan technique was employed for all data in the 2θ range of 20-54°. All reflections having $2\theta \leq 42^O$ were recorded. Reflections collected between 42° and 54° in 2θ were recorded only if a quick preliminary observation indicated a peak count five times the background count. The ω step-scan technique was employed for reflections recorded between 1^O and 21° in 2θ. The procedure of recording and processing data was almost identical with that followed in the work on TFPA, with the exceptions noted below.

All data were collected in the bisecting mode. In the $20-54^{\circ}$ range the total width of each 2θ scan was two degrees plus the width of the $\alpha_1-\alpha_2$ doublet separation. The step width was 0.05° in 2θ. The count time for each point in a scan was five seconds and the time for background counts taken at the beginning and end of each scan was twenty-five seconds. A niobium filter was used in recording reflections from $20-40^{\circ}$ in 2θ in order to eliminate the K_{β} line of molybdenum radiation; no filter was used in the $40-54^{\circ}$ range of 2θ. The takeoff angle at the X-ray tube was set at 1.5° in the range $20-42^{\circ}$ in 2θ and at 2.5° in the range $42-54^{\circ}$ in 2θ.

The total width of each ω scan was 0.60°. For both peak and background scans the step width was 0.025°, and the count time for each point was five seconds. No β-filter was used in the $1-21^{\circ}$ in 2θ range. The takeoff angle was set at 0.75° in the range 6 to 21° in 2θ and 0.50° in the range 1 to 6° in 2θ. Two different reference reflections were used, the 045 for $6-54^{\circ}$ in 2θ and the 321 for $1-7^{\circ}$ in 2θ. Two scale-factor identifiers were assigned, corresponding to the two reference reflections.

Absorption corrections were applied; the value of the absorption coefficient used was 49.04 cm^{-1}. The range of correction factors was from 2.56 to 3.23. The first derivatives of the transmission factor with respect to μ were also computed for subsequent use in extinction corrections.

A deck of reflection cards was prepared as for TFPA, one card for each reflection with punches for h, k, ℓ, F_O^2, $\sigma(F_O^2)$, the scale factor identifier, and $(dT/d\mu)/T$.

The value 5.67 $\overset{o}{A}{}^2$ for the over-all isotropic temperature factor B and an approximate value for the over-all scale factor on the F_O^2 values were obtained by the method of Wilson (11).

The normalized structure factors were computed, and statistical tests were applied to decide between the two space groups R3 and $\overline{R3}$. As Table III shows, there was a

TABLE III

EXPERIMENTAL DISTRIBUTION OF E VALUES FOR TIPA
COMPARED WITH THE THEORETICAL CENTRIC
AND ACENTRIC DISTRIBUTIONS

	Experimental	Theoretical (Centric)	Theoretical (Acentric)
Average magnitude of E	0.773	0.798	0.886
Average magnitude of E^2	1.000	1.000	1.000
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Percentage of E values greater than 1.00	28.03	32.00	37.00
Percentage of E values greater than 2.00	4.69	5.00	1.80
Percentage of E values greater than 3.00	0.86	0.30	0.01

positive indication that the space group is the centro-
symmetric one, $R\bar{3}$. Therefore, $R\bar{3}$ was assumed to be the
correct space group; the assumption was justified by the
subsequent analysis. On this assumption there are two
molecules of TIPA in the asymmetric unit, since there are
thirty-six molecules in the hexagonal cell, which has
eighteenfold general positions.

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CHAPTER III

STRUCTURE DETERMINATION AND REFINEMENT

Tri-(p-fluorophenyl)-amine

A direct method of phase determination was applied to
obtain the structural solution for TFPA. The phase signs
for 371 E values of magnitude greater than or equal to 1.50
were determined by a procedure for centrosymmetric struc-
tures embodied in R. E. Long's "Program for Sign Determi-
nation by Reiterative Application of Sayre's Equation" (12).
Sayre's equation (15) is

$$sE(\underset{\sim}{h}) \sim s\sum_{\underset{\sim}{h}'} E(\underset{\sim}{h}')E(\underset{\sim}{h}-\underset{\sim}{h}') \, ,$$

where s means "sign of" and the symbol ~ is to be read "is
probably equal to." The various E's corresponding to dif-
ferent reflections are distinguished by the index vectors
$\underset{\sim}{h}$, $\underset{\sim}{h}'$, and $\underset{\sim}{h}-\underset{\sim}{h}'$. The index vector $\underset{\sim}{h}$, representing a
reflection hkℓ, has components h, k, and ℓ; similarly,
$\underset{\sim}{h}-\underset{\sim}{h}'$ represents a reflection with indices h-h', k-k', and
ℓ-ℓ'. The E($\underset{\sim}{h}'$) and E($\underset{\sim}{h}-\underset{\sim}{h}'$) quantities on the right are
assumed to be signed quantities, the signs being just the
phase signs required for a Fourier synthesis (6) of the
centrosymmetric structure with the magnitudes F_o as Fourier
coefficients. The E's required on the right include not
only those calculated directly from the independent set of

F_o data recorded but also those calculated for the reflections equivalent by symmetry (13, 16) to those actually observed. For example, any $E(h,k,\ell) \equiv E(\underline{h})$ is represented in the expanded set also by: $E(\overline{h},\overline{k},\overline{\ell}) = E(h,k,\ell)$; $E(h,\overline{k},\ell) = \pm E(h,k,\ell)$; $E(\overline{h},k,\overline{\ell}) = \pm E(h,k,\ell)$ - where in the last two equations the plus sign applies if $h + k$ is even and the minus sign applies if $h + k$ is odd. Thus, for a given $E(\underline{h})$ whose sign is to be predicted, the summation is to be taken over all the pairs of known, signed E's of the expanded set whose index vectors add to give $\underline{h}$.

The Long program chooses the appropriate number of reflections to define an origin (3, 4) and n other reflections which with the origin-determining reflections serve as a starting set. The origin-determining signs are arbitrarily assigned and each of the other n signs may be plus or minus; therefore, 2^n possible starting sign sets are considered. When Sayre's equation is applied to a starting sign set, signs of additional reflections are predicted; these newly assigned signs are used to predict more signs and to redetermine the signs already predicted. For each of the 2^n starting sets this procedure is reiterated until there are no new additions or changes in the list of signed reflections for the particular set. The correct set is usually the one of the 2^n final sign sets with the highest consistency index c,

$$c \equiv \frac{\langle |E(\underline{h}) \sum_{\underline{h}'} E(\underline{h}')E(\underline{h}-\underline{h}')| \rangle}{\langle |E(\underline{h})| \sum_{\underline{h}'} |E(\underline{h}')||E(\underline{h}-\underline{h}')| \rangle}$$

where $\langle \ \rangle$ means the average over all values of $\underline{h}$. Usually this set also has the largest average value of $|(sigma)(E)|$, where sigma is the value of the sum in Sayre's equation; and usually it is the set which converged (that is, showed no further sign changes or additions) in the smallest number of cycles. The Long procedure is similar to the symbolic-addition procedure of Karle and Karle (8, 9). Unlike the latter procedure, however, it applies no probability criterion for acceptance of a given sign as correctly predicted before using that sign to predict others; and it uses no symbols other than plus and minus signs.

In the case of TFPA three reflections were chosen to fix the origin, as is appropriate for monoclinic symmetry, and four others were chosen to complete the starting set of reflections; there were, therefore, sixteen possible sign sets produced by the Long program. The set which appeared most probably correct by the criteria given above was indeed found to lead to the solution for the structure; in fact, the sign of each of the 371 E values as obtained by the program was found to be correct at the end of the structure determination.

A three-dimensional E map (8, 9) computed with the
signed E values of the most consistent solution as Fourier
coefficients clearly revealed the positions of the twenty-
two carbon, nitrogen, and fluorine atoms. The expression
used in calculating the three-dimensional Fourier summation
using the signed E values as coefficients was

$$\rho(x,y,z) = \frac{1}{V} \sum_{h} \sum_{k} \sum_{\ell} E(h,k,\ell) \cos 2\pi(hx + ky + \ell z),$$

where $\rho(x,y,z)$ is the electron density in electrons per $\overset{o}{A}{}^3$
at the point x,y,z in the cell and V is the volume of the
cell in $\overset{o}{A}{}^3$. The summation over each index is over the
entire range of values, positive, zero, and negative, that
appears in the expanded set of E values. From the coordi-
nates of the twenty-two atoms as taken from the initial E
map a structure-factor calculation was performed using the
equation

$$F_c(h,k,\ell) = \exp(-B(\sin\theta)^2/\lambda^2)$$
$$\times \sum_{j=1}^{N} f_j(h,k,\ell) \cos 2\pi(hx_j + ky_j + \ell z_j),$$

where $\exp(-B(\sin\theta)^2/\lambda^2)$ is the over-all isotropic tempera-
ture factor, f_j is the scattering factor for the atom j at
rest at the point x_j, y_j, z_j, and N is the total number of
atoms in the cell to be included. The scattering factors
used were from the compilation in the International Tables
(5). A conventional measurement of agreement between the
observed (F_o) and the calculated (F_c) structure factors is

described in terms of the residual or discrepancy index R(F), defined as

$$R(F) = \frac{\sum | |F_o| - |F_c| |}{\sum |F_o|}$$

where the summation is taken over all independent reflections. The residual for TFPA after this first structure-factor calculation was 0.32, sufficiently low to be taken as an indication of the probable correctness of the structure as obtained from the E map. Least-squares refinement was therefore started.

The quantity minimized in the least-squares refinement (2) was

$$\sum_{h,k,\ell} w(h,k,\ell) \left[|F_o(h,k,\ell)|^2 - |SF_c(h,k,\ell)|^2 \right]^2 ,$$

where $w(h,k,\ell)$ is the weight of the observation $|F_o(h,k,\ell)|^2$, and S is the parameter which scales the $|F_c(h,k,\ell)|$ values to the $|F_o(h,k,\ell)|$ values. The weight of each reflection was calculated by the equations

$$\sigma^2(F_o^2) = \sigma_s^2(F_o^2) + (0.03 \ F_o^2)^2 ,$$
$$w(F_o^2) = 1/\sigma^2(F_o^2) .$$

The correction term $(0.03 \ F_o^2)^2$ is added to the purely statistical variance $\sigma_s(F_o^2)$ to make some allowance for deficiencies in the structural model and for instability in the generator and counter circuitry (14).

Seven cycles of least-squares refinement of the over-all scale factor S, the over-all isotropic temperature parameter B, and the atomic coordinates were performed, resulting in a decrease of R(F) from 0.32 to 0.20. The starting value for S was $K^{-1/2}$, where K was the scale factor obtained by the Wilson method (see Chapter II); the starting value of B was also from the Wilson plot. After four cycles with an over-all scale factor and individual anisotropic thermal parameters (1) for the twenty-two carbon, nitrogen, and fluorine atoms, the residual index R(F) decreased to 0.10.

The expression for the anisotropic temperature factor (1) for a given atom j is

$$\beta_j(h,k,\ell) = \exp\left[-(b_j^{11}h^2 + b_j^{22}k^2 + b_j^{33}\ell^2 + 2b_j^{12}hk + 2b^{13}h\ell + 2b^{23}k\ell)\right],$$

and the structure-factor expression is

$$F_c(h,k,\ell) = \sum_{j=1}^{N} f_j(h,k,\ell)\beta_j(h,k,\ell)$$

$$\times \cos2\pi(hx_j + ky_j + \ell z_j),$$

where, as before, N is the number of atoms in the cell to be included. The symmetry relations among the β_j's of equivalent atoms have been discussed by Levy (10).

At this point in the refinement extinction corrections were applied for the first time. The least-squares program used allows the adjustment of the extinction parameter r*

of the general diffraction theory of Zachariasen (18, 19).
This parameter was adjusted in all subsequent cycles.
Hydrogen atoms were also introduced into the structure-
factor calculations at this point. The hydrogen atoms were
placed at approximately correct positions through use of a
computer program which makes use of general chemical-struc-
tural knowledge. For example, each hydrogen atom was
placed at the appropriate distance, about 1.0 $\overset{o}{A}$, from a
carbon atom along the bisector of the external angle at the
carbon. The thermal parameters originally assigned to the
hydrogen atoms were the same as those of the respective
carbon atoms to which they were attached. Neither the
coordinates nor the thermal parameters of the hydrogen atoms
were adjusted at this stage of the refinement. The residual
dropped to 0.050. The coordinates of the hydrogen atoms
were adjusted in the next cycle of refinement; R(F) remained
essentially the same.

In the next five cycles of least-squares refinement,
the four scale factors corresponding to the four scale-
factor identifiers were adjusted independently, along with
the coordinates and individual anisotropic temperature
factors of the twenty-two heavy atoms and the coordinates
and isotropic thermal parameters of the hydrogen atoms.
The value of R(F) dropped to 0.045. Finally, the individual
anisotropic thermal parameters of the hydrogen atoms were
refined along with all the other parameters of the previous

cycle, yielding a final value for R(F) of 0.044. The refinement was terminated when no further significant changes in any of the parameters appeared--specifically, when no shift of a parameter was greater than one tenth of its corresponding standard error.

Following the final least-squares refinement, a difference Fourier synthesis was calculated in order to see if the hydrogen atoms could actually be observed as peaks of electron density. A difference Fourier synthesis (11) is a synthesis in which the amplitudes are the differences between the observed and calculated structure factors:

$$\rho_o(x,y,z) - \rho_c(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_\ell (F_o - F_c)$$

$$x \cos 2\pi(hx + ky + \ell z) \ .$$

For the purpose of locating the hydrogen atoms, the signed values F_c used in this expression included contributions from all the atoms except the hydrogen atoms, but the signs attached to the F_o's were from a structure-factor calculation in which all atoms were included. Thus, in principle the carbon, nitrogen, and oxygen peaks were "subtracted" from the density map; only peaks corresponding to hydrogen atoms and residual peaks attributable to errors in the model and in the data should have been left. In fact, all of the hydrogen atoms were located in this map, at the positions of highest density (0.66 to 0.44 electrons per $\overset{o}{A}{}^3$). Another difference synthesis in which all atoms were

subtracted showed residual troughs and peaks from -0.24 to 0.15 electrons per $\overset{o}{A}{}^3$. Such a residual map is satisfactory according to the usual standards.

The final atomic parameters and their standard errors appear in Table IV. The final value of Zachariasen's extinction parameter r^* is 9.23 x 10^{-6} (σ = 0.85 x 10^{-6})cm. A listing of the final observed and calculated structure factors is given in Table V. The values of the extinction corrections are indicated approximately in Table V according to the following letter code:

blank $>$ 0.995

0.995 $\geq$ A $\geq$ .990

.990 $>$ B $\geq$ .980

.980 $>$ C $\geq$ .970

.970 $>$ D $\geq$ .960

.960 $>$ E $\geq$ .950

.950 $>$ F $\geq$ .925

.925 $>$ G $\geq$ .900

.900 $>$ H $\geq$ .875

.875 $>$ I $\geq$ .850

.850 $>$ J $\geq$ .825

.825 $>$ K $\geq$ .800

.800 $>$ L $\geq$ .775

.775 $>$ M $\geq$ .750

.750 $>$ N $\geq$ .725

.725 $>$ O $\geq$ .700

TABLE IV

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS OF THE CRYSTAL STRUCTURE OF TRI-(p-FLUOROPHENYL)-AMINE (WITH STANDARD ERRORS IN PARENTHESES)

	Fractional Coordinates x 10^5			Thermal Parameters x 10^5					
	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
Ring 1									
N	50258(9)	12658(7)	92142(13)	802(11)	555(5)	2040(21)	-99(5)	606(11)	-298(8)
C(1)	40050(10)	09434(6)	78483(14)	852(12)	372(4)	1758(21)	-48(5)	533(11)	-16(7)
C(2)	43100(12)	03379(7)	69633(15)	1032(13)	401(5)	1855(23)	-7(6)	593(13)	-35(8)
C(3)	33249(14)	00111(9)	56297(18)	1373(16)	479(6)	1963(26)	-139(7)	756(16)	-172(9)
C(4)	20335(13)	02965(9)	52143(16)	1184(15)	599(6)	1665(22)	-246(7)	414(14)	-77(9)
C(5)	16940(13)	08911(9)	60555(17)	890(13)	540(6)	2076(26)	-33(7)	376(14)	152(10)
C(6)	26854(11)	12230(8)	73674(17)	899(12)	394(5)	2282(26)	1(6)	559(13)	14(9)
F	10582(9)	-00228(7)	39121(11)	1531(13)	1010(6)	2254(19)	-410(7)	244(11)	-435(8)
Ring 2									
C(1)	63918(10)	12519(7)	91969(14)	822(12)	410(4)	1814(21)	-70(5)	572(11)	-131(7)
C(2)	73721(13)	08627(8)	104180(19)	1102(14)	507(6)	1977(26)	-14(7)	527(15)	56(9)
C(3)	86951(14)	08491(10)	103950(21)	989(15)	615(7)	2556(32)	95(8)	374(16)	-61(12)
C(4)	89916(13)	12260(9)	91477(20)	887(13)	609(7)	2950(33)	-102(7)	826(17)	-355(12)
C(5)	80494(15)	16100(9)	79202(21)	1377(17)	566(7)	2568(31)	-186(8)	1163(20)	-89(11)
C(6)	67258(14)	16266(8)	79493(19)	1133(15)	481(6)	2044(26)	-15(7)	648(15)	47(9)
F	102841(8)	12139(7)	91246(15)	985(11)	1059(7)	4637(31)	-144(6)	1315(14)	-540(11)
Ring 3									
C(1)	47584(10)	15544(7)	106318(15)	885(12)	399(4)	1786(21)	10(5)	546(12)	-49(7)
C(2)	37185(12)	12619(8)	111563(17)	1025(13)	407(5)	2234(26)	12(6)	723(14)	53(9)
C(3)	34771(14)	15583(9)	125472(18)	1212(15)	558(6)	2137(27)	182(8)	910(16)	227(10)
C(4)	42864(15)	21382(10)	134070(17)	1445(17)	629(7)	1759(24)	239(9)	706(16)	-36(10)
C(5)	53288(17)	24277(10)	129468(21)	1581(20)	608(7)	2292(31)	-76(9)	744(19)	-371(12)
C(6)	55592(15)	21389(9)	115493(18)	1270(15)	519(6)	2226(27)	-168(7)	821(16)	-240(10)
F	40353(11)	24355(7)	147666(11)	2115(16)	1035(6)	2151(19)	275(8)	1119(13)	-318(8)

TABLE IV--Continued

	Fractional Coordinates x 10^5			Thermal Parameters x 10^5					
	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
Ring 1									
H(2)	5244(13)	0127(7)	7299(16)	89(16)	48(6)	253(30)	14(8)	43(18)	-17(11)
H(3)	3556(16)	0424(10)	5005(21)	191(25)	71(8)	314(41)	-13(12)	103(26)	-61(16)
H(5)	0768(16)	1078(9)	5710(17)	120(19)	75(8)	230(31)	10(11)	26(20)	16(13)
H(6)	2473(13)	1657(8)	7993(18)	137(20)	40(6)	304(36)	14(9)	84(21)	-34(12)
Ring 2									
H(2)	7135(16)	0623(10)	11321(17)	197(24)	91(9)	118(24)	13(12)	75(20)	36(12)
H(3)	9432(19)	0586(10)	,11317(26)	196(28)	81(10)	392(47)	27(14)	89(29)	12(18)
H(5)	8324(18)	1882(9)	7050(21)	257(30)	70(8)	271(36)	7(13)	167(28)	36(14)
H(6)	6024(15)	1900(9)	7116(19)	144(22)	76(9)	204(31)	17(11)	54(20)	51(13)
Ring 3									
H(2)	3166(15)	0845(8)	10554(22)	153(21)	49(6)	399(42)	-35(10)	191(25)	-42(14)
H(3)	2757(15)	1382(9)	12917(17)	157(22)	81(9)	219(30)	-4(11)	109(22)	24(13)
H(5)	5951(20)	2821(11)	13642(21)	225(30)	92(10)	277(39)	-25(14)	77(28)	-92(18)
H(6)	6318(15)	2338(9)	11200(18)	145(22)	76(8)	279(34)	-52(11)	98(23)	-58(14)

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS (x 10) FOR TRI-(p-FLUOROPHENYL)-AMINE, WITH STANDARD ERRORS (SEE TEXT FOR EXPLANATION)

TABLE V--Continued

$$0.700 > P \geq 0.675$$

$$.675 > Q \geq .650$$

The standard error $\sigma(F_O)$, computed as $\sigma(F_O^2)/2F_O$, is given

for each reflection for which $F_O^2 > \sigma(F_O^2)$; the error $\sigma(F_O^2)$

is given for each reflection (marked W) for which

$F_O^2 \leq \sigma(F_O^2)$. The symbol R marks a few reflections having

$|F_O^2 - F_C^2|/\sigma(F_O^2) \geq 8$ which were excluded in the final least-

squares cycles. The F_O and F_C values as given in Table V

are scaled up by a factor of ten over the scale established

in the refinement. The $\sigma(F_O)$ and $\sigma(F_O^2)$ values are scaled

up by a factor of one hundred. The value $10F_O(041)$, given

as zero to save space in the Table, is really 1104.

Tri-(p-iodophenyl)-amine

The strong indication from the statistical analysis of

the E values that the space group of TIPA is centrosymmetric

suggested the application of R. E. Long's program for the

solution of the phase problem for centrosymmetric struc-

tures. The 534 E values greater than or equal to 1.50 were

used as input into the Long program. For use in the Long

program the rhombohedral primitive-lattice description of

the crystal was required. Hence, for this purpose only,

the reflection indices were transformed by the appropriate

matrix equation,

$$\begin{vmatrix} h' \\ k' \\ \ell' \end{vmatrix} = \begin{vmatrix} 2/3 & 1/3 & 1/3 \\ -1/3 & 1/3 & 1/3 \\ -1/3 & -2/3 & 1/3 \end{vmatrix} \begin{vmatrix} k \\ k \\ \ell \end{vmatrix}$$

corresponding to transformation from the hexagonal cell to the obverse rhombohedral cell with

$$a = b = c = 25.839 \overset{\text{o}}{\text{A}}$$

$$\alpha = \beta = \gamma = 118.32^{\text{o}}$$

An E map based upon the best sign combination for the 534 E values, chosen according to the same criteria as used for TFPA, contained six outstanding peaks which could rationally be identified with the six iodine atoms of the asymmetric unit. The phases of the entire set of 534 E values were later shown to be correct.

A structure-factor calculation based upon the six iodine atoms found in the E map yielded an R(F) value of 0.44. A difference Fourier synthesis (with the iodine atoms subtracted) was computed in hopes of finding some or all of the thirty-eight nitrogen and carbon atoms; however, because of some gross errors in the calculation of this first difference map, no nitrogen or carbon atoms could be located. Because of these errors, not recognized at the time, a new procedure was tried. The assumption was made that the three iodine atoms of a single molecule should describe an equilateral triangle with the nitrogen atom at its centroid, that is, that the nitrogen valence angles must have plane trigonal geometry. The two nitrogen atoms were therefore placed at the centroids of two approximately equilateral triangles described by two sets of three iodine atoms. For each ring approximate coordinates for the two

carbon atoms which could be assumed to lie nearly along the line between a nitrogen atom and an iodine atom were also calculated. The iodine atom positions and their anisotropic thermal parameters were subjected to a least-squares refinement, the same quantity

$$\sum_{h,k,\ell} w(h,k,\ell) \left[|F_o(h,k,\ell)|^2 - |SF_c(h,k,\ell)|^2 \right]^2$$

being minimized as in the refinement of TFPA. The thermal and positional parameters of the fourteen carbon and nitrogen atoms were held constant. The R(F) value decreased to 0.28 after two cycles of refinement.

A correctly computed difference Fourier map (with only the iodine atoms subtracted) revealed all but one of the thirty-eight nitrogen and carbon atoms, including the fourteen atoms inserted previously from geometrical considerations. The weighting scheme of Woolfson (17) was employed in computing the coefficients for this difference Fourier synthesis; the weight w used with each coefficient F_o-F_c was

$$w = \tanh \frac{|F_o F_c|}{\epsilon[\exp-2B(\sin\theta)^2/\lambda^2]\sum f_j^2},$$

where the sum is over all atoms in the cell except the iodine atoms, F_o is the observed structure factor, F_c is the calculated structure factor for the iodine atoms only, and the factor ϵ has been explained previously (Chapter II) in the definition of the normalized structure factor. The

weight thus calculated represents P_+-P_-, where P_+ is the probability that F_o and F_c have the same sign and P_- is the probability that they have opposite signs.

Approximate coordinates of the single unlocated carbon atom were calculated, assuming a regular-hexagonal benzene ring. In the third least-squares cycle the usual nine parameters of each of the six iodine atoms, the coordinates of the thirty-eight light atoms, and one over-all scale factor were refined. The residual decreased to 0.18. In the fourth cycle individual isotropic temperature factors for the carbon and nitrogen atoms were introduced and refined, along with those parameters already mentioned for the third cycle. The extinction parameter was introduced and refined along with the usual nine parameters of each of the forty-four atoms in the next two cycles, with an accompanying decrease in $R(F)$ to 0.12. Hydrogen atoms in fixed calculated positions were included in the seventh cycle of refinement. The added hydrogen atoms had virtually no effect upon the refinement of the parameters of other atoms or on $R(F)$; they were therefore omitted from further least-squares refinement.

The ten extra parameters of the three-cumulant model (7) were adjusted for each iodine atom in the last five cycles of refinement. The usual six-parameter anisotropic temperature factor is appropriate strictly only for harmonic motions along rectilinear paths. The ten extra

parameters of the three-cumulant model make allowance for curvilinear or librational motions. The memory size of the computer permitted application of the three-cumulant model only to the iodine atoms. These are, of course, the atoms for which it is most useful to apply the model, because they are the heaviest scatterers in the structure and because in their peripheral positions in the molecules they show the largest librational displacements.

The dispersion corrections (5) for iodine, $\Delta f' = -0.5$ and $\Delta f'' = 2.3$, were also included in these last cycles. The complex structure-factor equation used was

$$F_c(\underline{h}) = A(\underline{h}) + i\, B(\underline{h}) \; ,$$

where

$$A(\underline{h}) = \sum_{r=1}^{N} \beta_r(\underline{h})\{f'_r(\underline{h})\cos[\alpha_r(\underline{h})] - f''_r(\underline{h})\sin[\alpha_r(\underline{h})]\},$$

$$B(\underline{h}) = \sum_{r=1}^{N} \beta_r(\underline{h})\{f'_r(\underline{h})\sin[\alpha_r(\underline{h})] + f''_r(\underline{h})\cos[\alpha_r(\underline{h})]\},$$

and

$$\alpha_r(\underline{h}) = 2\pi \sum_{i=1}^{3} x^i_r h_i - \sum_{i,j,k}^{3} c^{ijk}_r h_i h_j h_k \; ,$$

$$\beta_r(\underline{h}) = \exp(-\sum_{i,j=1}^{3} b^{ij}_r h_i h_j) \; .$$

The last two equations are in tensor notation, where x^1, x^2, x^3 replace x, y, z and h_1, h_2, h_3 replace h, k, ℓ. $\beta_r(\underline{h})$ is the same anisotropic temperature factor previously defined, with six independent terms b^{ij}. There are ten

independent c^{ijk} terms. The symbol f' denotes the real part of the complex scattering factor, which is just the tabulated factor (5) for every kind of atom except iodine, for which f' includes also the Δf' value specified above. The symbol f'' is the imaginary part of the scattering factor, which is the Δf'' as given above for iodine and zero for all other atoms.

In the first four cycles using the three-cumulant model the parameters of only half of the asymmetric unit could be refined in one cycle because of the limited fast-core memory of the IBM 360/75 computer. Later, the parameters of the entire asymmetric unit were refined at once on the IBM 360/91. The final R(F) value was 0.098. A difference map calculated after the final least-squares calculation revealed the largest positive residual electron ensity to be 1.88 electrons $\overset{o}{A}^{-3}$ and the largest negative value to be -1.96 electrons $\overset{o}{A}^{-3}$. These values of the residual electron density, although higher than those for TFPA, are acceptable when one considers the presence of the heavy iodine atoms.

After the complete structure had been solved, a review of the calculation of the first difference map revealed the errors made. Subsequently a correct calculation of this difference map showed the location of most of the light atoms.

The final atomic parameters and their standard errors appear in Table VI. The final value of Zachariasen's

TABLE VI

FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS OF THE CRYSTAL STRUCTURE OF TRI-(p-IODOPHENYL)-AMINE (WITH STANDARD ERRORS IN PARENTHESES)

Molecule 1	Fractional Coordinates x 10^5			Thermal Parameters x 10^5					
	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
Ring 1									
N	24997(24)	36525(24)	09558(95)	78(10)	63(9)	1036(130)	44(8)	31(29)	-1(29)
C(1)	26085(29)	34169(29)	05256(114)	60(11)	60(11)	924(150)	30(9)	90(33)	37(33)
C(2)	28051(29)	33318(31)	13858(111)	71(11)	98(13)	972(159)	60(11)	-13(34)	-77(37)
C(3)	29141(32)	30943(31)	09339(118)	104(14)	83(13)	898(155)	52(11)	-22(38)	-63(35)
C(4)	28208(30)	29633(27)	-03455(117)	79(12)	44(10)	1013(157)	30(9)	100(36)	-49(32)
C(5)	26306(31)	30471(30)	-11935(113)	85(13)	73(12)	882(153)	43(10)	-27(35)	44(34)
C(6)	25230(29)	32013(28)	-07533(109)	78(12)	57(11)	829(143)	39(9)	29(33)	-23(31)
I	29782(5)	26158(4)	-10083(16)	180(1)	124(1)	1427(14)	114(1)	48(3)	-52(3)
Ring 2									
C(1)	25391(31)	39260(30)	01104(110)	78(12)	56(11)	799(141)	29(10)	-7(34)	24(31)
C(2)	28237(31)	40679(31)	-07566(122)	79(13)	69(12)	1086(177)	20(10)	112(38)	73(37)
C(3)	28573(32)	43319(33)	-16181(122)	89(13)	89(13)	1168(178)	51(11)	-48(39)	-90(38)
C(4)	26206(33)	44553(28)	-15352(108)	92(13)	65(11)	610(136)	36(10)	-32(34)	-34(31)
C(5)	23450(32)	43208(31)	-06423(108)	82(12)	79(12)	627(133)	37(10)	-43(33)	5(33)
C(6)	22993(30)	40389(29)	01643(108)	85(12)	62(11)	772(144)	36(10)	-72(34)	-94(31)
I	26880(4)	48679(4)	-27434(14)	148(1)	120(1)	989(11)	82(1)	29(3)	111(3)
Ring 3									
C(1)	23697(31)	36226(31)	22798(110)	81(12)	79(12)	793(140)	67(11)	20(33)	-7(34)
C(2)	24940(28)	39283(30)	30090(111)	67(11)	76(11)	868(149)	47(10)	11(33)	-21(34)
C(3)	23649(28)	39117(29)	43122(116)	62(11)	66(11)	1055(158)	40(9)	-33(33)	7(34)
C(4)	21200(28)	35799(31)	47897(104)	61(11)	81(12)	564(127)	43(10)	12(29)	36(31)
C(5)	19992(32)	32765(31)	40525(119)	105(14)	71(12)	953(157)	55(11)	-33(38)	-8(36)
C(6)	21259(30)	32944(28)	27586(121)	73(12)	42(10)	1156(164)	22(9)	40(35)	8(33)
I	19209(4)	35501(4)	67036(14)	104(1)	124(1)	832(10)	53(1)	30(3)	9(3)

TABLE VI--Continued

Molecule 2

	Fractional Coordinates x 10⁵			Thermal Parameters x 10⁵					
	x	y	z	b^{11}	b^{22}	b^{33}	b^{12}	b^{13}	b^{23}
Ring 1									
N	27075(25)	50964(24)	23549(93)	78(10)	79(10)	1030(134)	51(8)	100(29)	142(29)
C(1)	24233(31)	49286(31)	32424(121)	67(12)	66(12)	1073(170)	34(10)	31(35)	84(36)
C(2)	22256(29)	45675(29)	32312(117)	51(10)	55(11)	1243(171)	17(9)	-25(33)	54(34)
C(3)	19513(31)	43922(33)	41870(121)	64(11)	107(14)	1119(172)	50(11)	20(36)	-4(39)
C(4)	19010(30)	46115(34)	50417(121)	61(12)	87(13)	1196(180)	40(11)	83(36)	175(40)
C(5)	20796(31)	49733(33)	50107(110)	79(12)	96(13)	824(156)	57(11)	-2(34)	74(36)
C(6)	23551(30)	51424(29)	40690(111)	76(12)	71(11)	861(149)	51(10)	-58(33)	-22(33)
—	15156(5)	43589(5)	64881(20)	154(1)	194(2)	2385(20)	124(1)	398(4)	405(4)
Ring 2									
C(1)	29503(26)	49757(26)	22837(107)	32(9)	45(9)	875(138)	9(8)	-16(28)	9(29)
C(2)	31083(26)	49774(27)	10880(102)	39(9)	68(11)	845(137)	26(8)	80(28)	9(31)
C(3)	33442(31)	48549(30)	10889(120)	76(12)	70(12)	1199(184)	37(10)	46(37)	48(36)
C(4)	34138(31)	47402(31)	22835(144)	78(13)	86(13)	1805(231)	48(11)	112(44)	219(46)
C(5)	32601(34)	47327(28)	34696(122)	98(14)	46(10)	1104(171)	23(10)	75(9)	69(4)
C(6)	30326(29)	48626(30)	34675(116)	65(11)	57(11)	1141(164)	23()	-50(35)	44(4)
—	37617(7)	45467(8)	21807(27)	242(2)	358(2)	3902(30)	264(2)	592(6)	780(7)
Ring 3									
C(1)	26986(32)	53087(30)	13201(109)	72(11)	72(12)	818(149)	50(10)	100(33)	91(32)
C(2)	23983(30)	51906(31)	06100(116)	80(12)	102(14)	897(152)	68(11)	28(35)	26(37)
C(3)	23840(31)	54040(34)	-04074(117)	81(12)	94(13)	1008(61)	55(11)	143(37)	25(38)
C(4)	26904(36)	57354(34)	-06375(116)	106(14)	105(14)	911(160)	81(13)	114(39)	80(39)
C(5)	29973(34)	58545(32)	00544(133)	86(13)	91(14)	1498(208)	55(12)	31(41)	123(42)
C(6)	30020(31)	56281(31)	10734(120)	76(12)	65(12)	1148(173)	22(10)	20(36)	100(35)
—	26663(4)	60560(5)	-20971(16)	165(1)	177(1)	1383(14)	137(1)	194(3)	247(3)

TABLE VI--Continued

Components of Third-Cumulant Tensor x 10^6 (For Iodine Atoms Only)

	c^{111}	c^{222}	c^{333}	c^{112}	c^{122}	c^{113}	c^{133}	c^{223}	c^{233}	c^{123}
Molecule 1										
Ring 1	1(1)	5(1)	-88(29)	4(1)	5(1)	-13(2)	-22(5)	-5(1)	-6(5)	-7(1)
Ring 2	-6(1)	-2(1)	17(20)	-4(1)	-2(1)	0(1)	-2(4)	-3(1)	5(4)	0(1)
Ring 3	-1(1)	-3(1)	-20(20)	-1(1)	-1(1)	-1(1)	-2(4)	0(1)	-6(4)	1(1)
Molecule 2										
Ring 1	8(1)	28(1)	224(49)	12(1)	18(1)	28(2)	89(9)	64(3)	144(9)	43(2)
Ring 2	-8(1)	-2(2)	1057(94)	-6(1)	-5(2)	19(4)	192(16)	48(5)	291(19)	29(4)
Ring 3	0(1)	-9(1)	-39(29)	-1(1)	-4(1)	3(2)	-3(6)	-9(2)	-13(6)	-2(2)

extinction parameter r^* is 5.14 x 10^{-6} (σ = 0.34 x 10^{-6})cm. A listing of the final observed and calculated structure factors is given in Table VII. The indices refer to the hexagonal cell. The F_c values include the computed extinction corrections; the signs are the signs of the real parts of the complex F_c's. The values of the extinction corrections are indicated approximately in Table VII according to the same letter code used for TFPA. The standard error $\sigma(F_O)$, computed as $\sigma(F_O^2)/2F_O$, is given for each reflection for which $F_O^2 > \sigma(F_O^2)$; the error $\sigma(F_O^2)$ is given for each reflection (marked W) for which $F_O^2 \leq \sigma(F_O^2)$. The symbol R marks the 030 reflection for which $|F_O^2-F_c^2|/\sigma(F_O^2) > 10$ and weak reflections for which $(\sin\theta)/\lambda$ is greater than 0.504 and for which $F_O^2 \leq 3\sigma(F_O^2)$. All reflections marked R were excluded from the final least-squares cycles. The values of F_O, F_c, and $\sigma(F_O^2)$ as given in Table VII have been scaled down by the factor 0.1 from the absolute scale established by the refinement; the values of $\sigma(F_O)$ are on the absolute scale.

TABLE VII

OBSERVED AND CALCULATED STRUCTURE FACTORS (x 0.10)
FOR TRI-(p-IODOPHENYL)-AMINE, WITH STANDARD
ERRORS (SEE TEXT FOR FULL EXPLANATION)

TABLE VII--Continued

TABLE VII--Continued

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CHAPTER IV

DISCUSSION AND CONCLUSION

Thermal Motion

All the information about thermal motion which is
available for TFPA from the least-squares crystal-structure
analysis is contained in the sets of thermal parameters b_r^{ij}
of the various atoms r. The six b_r^{ij}'s of atom r are the
unique components of a symmetric second-rank tensor $\underset{\sim}{b}_r$;
they are contravariant components in terms of the base
vectors $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$, $\underset{\sim}{a}_3$ of the crystal lattice. For the purpose
of interpreting the thermal motion, it is useful to perform
a principal-axis transformation (4, 14, 25) on the quadratic
form $\underset{\sim}{h}^t \underset{\sim}{b}_r \underset{\sim}{h}$ which appears as the exponent in the temperature
factor of each atom r. One can then compute the directions
of each principal axis and the root-mean-square displace-
ments along each axis. Table VIII gives for TFPA these
root-mean-square displacements. Figure 2 gives both the
displacements and the orientations by presenting the so-
called fifty per cent probability ellipsoids of Johnson
(13, 14). These ellipsoids have their principal axes along
the principal axes of the $\underset{\sim}{b}_r$ tensors and are scaled so that
the distance from the center to the surface along a princi-
pal axis is 1.54 times the root-mean-square amplitude in
the axial direction. Table VIII and Figure 2 seem generally

TABLE VIII

ROOT-MEAN-SQUARE AMPLITUDES (Å) OF VIBRATION IN THE
PRINCIPAL-AXIS DIRECTIONS FOR THE ATOMS IN THE
TRI-(p-FLUOROPHENYL)-AMINE STRUCTURE

Atoms	Ring 1			Ring 2			Ring 3		
	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3
N	0.185(1)	0.230(1)	0.315(1)						
C(1)	.192(1)	.237(1)	.244(1)	0.187(2)	0.228(1)	0.267(1)	0.197(1)	0.239(2)	0.252(1)
C(2)	.213(2)	.244(2)	.254(2)	.230(2)	.253(2)	.281(2)	.207(2)	.248(2)	.275(2)
C(3)	.228(2)	.242(2)	.297(2)	.218(2)	.289(2)	.316(2)	.202(2)	.249(2)	.319(2)
C(4)	.219(2)	.236(2)	.320(2)	.190(2)	.264(2)	.347(2)	.212(2)	.258(2)	.330(2)
C(5)	.209(2)	.251(2)	.300(2)	.198(2)	.282(2)	.323(2)	.233(2)	.276(2)	.335(2)
C(6)	.205(2)	.245(1)	.274(2)	.223(2)	.260(2)	.274(2)	.223(2)	.243(2)	.313(2)
F	.220(1)	.309(1)	.413(1)	.184(1)	.344(1)	.442(1)	.208(1)	.324(1)	.416(1)
H(2)	.19(2)	.26(2)	.31(2)	.16(2)	.31(2)	.38(2)	.17(2)	.25(2)	.40(2)
H(3)	.24(2)	.30(2)	.39(2)	.29(2)	.36(2)	.37(2)	.20(2)	.30(2)	.36(2)
H(5)	.23(2)	.29(2)	.34(2)	.22(2)	.33(2)	.38(2)	.21(2)	.34(2)	.43(2)
H(6)	.19(2)	.28(2)	.34(2)	.22(2)	.27(2)	.37(2)	.21(2)	.26(2)	.40(2)
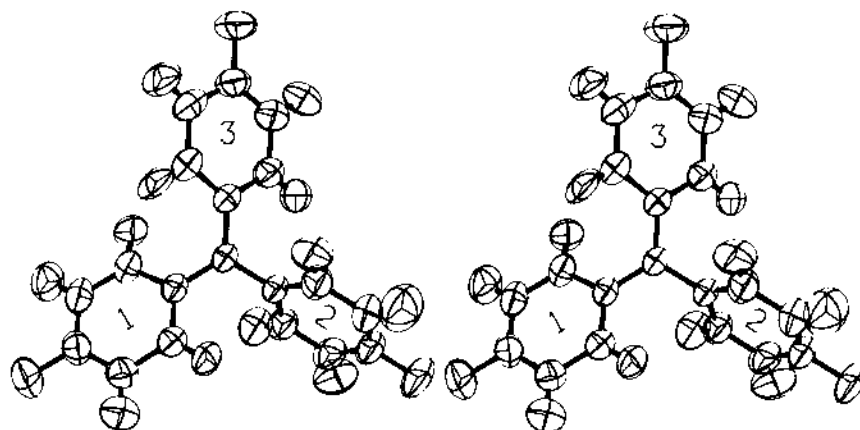
Fig. 2--The fifty per cent probability thermal ellip-
soids from the thermal parameters of tri-(p-fluorophenyl)-
amine. View direction is normal to the plane of the three
carbons attached to nitrogen.

sensible on inspection; there are no obvious inconsistencies
in ellipsoid shapes or orientations, and the atomic vibra-
tional amplitudes generally increase from the center to the
periphery of the molecule, the fluorine atoms having the
largest amplitudes.

For molecules which are rigid or which are made up of
rigid segments more elaborate analyses are often useful
because thermal motion is interesting in itself and because
corrections to apparent bond lengths and angles for perturb-
ing effects of thermal motion can be obtained. The effects
of thermal motion are such that apparent bond lengths
calculated from the atomic coordinates are always shorter
than the true mean separations; apparent valence angles may
be in error in either direction (5, 6, 15).

Cruickshank (6, 7, 8) developed a method for analyzing the rigid-body motion of molecules in terms of two symmetric tensors, a translational tensor $\underset{\sim}{T}$ and a librational tensor $\underset{\sim}{L}$. Although it was not recognized until much later, this description is inadequate for molecules which do not lie on a center of symmetry. A general method for determining the rigid-body motion was developed by Schomaker and Trueblood (21), who introduced an additional tensor $\underset{\sim}{S}$ to take account of correlations of librational and translational motion. The explanation which follows is based on a restatement by Johnson (13) of their arguments in simpler notation.

A rigid body is defined as a system of particles constrained to maintain constant interparticle separations. A rigid motion is any transformation of the rigid body which leaves the interparticle distances unchanged. All of the available information about such motion is contained in the tensors $\underset{\sim}{b}_r$. For convenience, each $\underset{\sim}{b}_r$ is transformed to an "observed" tensor $\underset{\sim}{U}_r^O$ with components referred to a set of unit Cartesian base vectors $\underset{\sim}{i}_1$, $\underset{\sim}{i}_2$, $\underset{\sim}{i}_3$ such that the atomic mean-square amplitude of vibration $\overline{u_r^2}$ in the direction of a unit vector $\underset{\sim}{\ell}$ with direction cosines ℓ_1, ℓ_2, ℓ_3 is given by

$$\overline{u_r^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij,r}^O \ell_i \ell_j = \underset{\sim}{\ell}^t \underset{\sim}{U}_r^O \underset{\sim}{\ell} \, ,$$

where the superscript t denotes the transpose of the matrix

$\underline{\ell}$. The Cartesian base vectors are usually defined in terms of intramolecular axes. It may be shown that the desired tensor $\underline{U}_r^O$ is given by

$$\underline{U}_r^O = (1/2\pi^2)(\underline{E}^t\underline{D}^t\underline{b}_r\underline{D}\,\underline{E}), \qquad [1]$$

where

$$\underline{D} \equiv \begin{bmatrix} 1/a_1^* & 0 & 0 \\ 0 & 1/a_2^* & 0 \\ 0 & 0 & 1/a_3^* \end{bmatrix} \equiv \underline{D}^t,$$

and $\underline{E}^t$ is the matrix which transforms a set of unit base vectors $\underline{i}_1',\underline{i}_2',\underline{i}_3'$ oriented along the reciprocal axes $\underline{a}_1^*,\underline{a}_2^*,$ $\underline{a}_3^*$ to the Cartesian base vectors $\underline{i}_1,\underline{i}_2,\underline{i}_3$, that is,

$$\begin{bmatrix} \underline{i}_1 \\ \underline{i}_2 \\ \underline{i}_3 \end{bmatrix} = \underline{E}^t \begin{bmatrix} \underline{i}_1' \\ \underline{i}_2' \\ \underline{i}_3' \end{bmatrix}.$$

The simplest general treatment of rigid-body motion is obtained in terms of first-order instantaneous displacement parameters in translation $\underline{t}$ and rotation $\underline{\lambda}$. In this approximation the displacement $\underline{u}$ of an atom from its equilibrium position $\underline{r}$ is

$$\underline{u} = \underline{t} + \underline{\lambda} \times \underline{r} = \underline{t} + \underline{A}\,\underline{\lambda}, \qquad [2]$$

where the symbol x denotes the vector cross product and

$$\underline{A} = \begin{bmatrix} 0 & r_3 & -r_2 \\ -r_3 & 0 & r_1 \\ r_2 & -r_1 & 0 \end{bmatrix}.$$

The calculated tensor $\underline{U}_r^C$ for the particular atom r is

obtained by taking the direct product of the vector $\underset{\sim}{u}$ with itself, defined as $\underset{\sim}{u}\,\underset{\sim}{u}^t$ in matrix notation (10), and averaging each term of the resulting 3 x 3 matrix over time and lattice, that is,

$$\underset{\sim}{U}_r^c \equiv \langle \underset{\sim}{u}\,\underset{\sim}{u}^t \rangle \equiv [\overline{u_i u_j}] ,$$

where the brackets $\langle \; \rangle$ denote the averaging of the individual elements of $\underset{\sim}{u}\,\underset{\sim}{u}^t$. Expansion of $\underset{\sim}{u}$ and $\underset{\sim}{u}^t$ according to equation [2] gives

$$\langle \underset{\sim}{u}\,\underset{\sim}{u}^t \rangle = \langle \underset{\sim}{t}\,\underset{\sim}{t}^t \rangle + \langle \underset{\sim}{A}\,\underset{\sim}{\lambda}\,\underset{\sim}{\lambda}^t\underset{\sim}{A}^t \rangle + \langle \underset{\sim}{t}\,\underset{\sim}{\lambda}^t\underset{\sim}{A}^t \rangle + \langle \underset{\sim}{A}\,\underset{\sim}{\lambda}\,\underset{\sim}{t}^t \rangle ,$$

or

$$\underset{\sim}{U}_r^c = \underset{\sim}{T} + \underset{\sim}{A}\,\underset{\sim}{L}\,\underset{\sim}{A} + \underset{\sim}{A}\,\underset{\sim}{S} + \underset{\sim}{S}^t\underset{\sim}{A}^t , \qquad [3]$$

where

$$\underset{\sim}{L} = [\overline{\lambda_i \lambda_j}] ,$$
$$\underset{\sim}{S} = [\overline{\lambda_i t_j}] ,$$
$$\underset{\sim}{S}^t = [\overline{t_i \lambda_j}] ,$$

and

$$\underset{\sim}{T} = [\overline{t_i t_j}] .$$

The symmetric tensor $\underset{\sim}{T}$ describes the translational vibrational motion, and the screw tensor $\underset{\sim}{S}$ accounts for correlations of libration and translation. The inclusion of the $\underset{\sim}{S}$ tensor in the rigid-body analysis makes $\underset{\sim}{L}$ and the fit of observed and calculated $\underset{\sim}{U}$'s independent of origin, although the components of $\underset{\sim}{S}$ and $\underset{\sim}{T}$ vary with the origin.

The $\underset{\sim}{U}_r^c$'s of the various atoms r calculated according to equation [3] are the calculated tensors corresponding to the "observed" $\underset{\sim}{U}_r^o$ of equation [1]. The whole set of

elements $U^c_{ij,r}$ for all the atoms are fitted to the $U^o_{ij,r}$ by least-squares adjustment of the independent elements of $\underset{\sim}{T}$, $\underset{\sim}{L}$, and $\underset{\sim}{S}$. There are in general six independent elements each for $\underset{\sim}{T}$ and $\underset{\sim}{L}$ and eight independent elements for $\underset{\sim}{S}$, making a total of twenty parameters to be determined.

For a description relative to a set of intersecting axes, a condition for maximum decoupling of the mean-square translational and vibrational motion is that the trace of $\underset{\sim}{T}$ be minimized and that $\underset{\sim}{S}$ be simultaneously symmetrized. The tensors $\underset{\sim}{S}$, $\underset{\sim}{T}$, and $\underset{\sim}{L}$ can be defined in terms of any arbitrary initial origin, usually the mass center of the molecule. Then a unique shift of origin can be brought about which minimizes the trace of $\underset{\sim}{T}$ and simultaneously makes $\underset{\sim}{S}$ symmetric. The origin which minimizes the trace of $\underset{\sim}{T}$ and $\underset{\sim}{S}$ symmetric is called the reaction center. A further reduction in the trace of $\underset{\sim}{T}$ and an annihilation of the off-diagonal coefficients of $\underset{\sim}{S}$ is possible if the rigid-body orientations are described in terms of three nonintersecting axes of libration, each along one of the principal directions of libration. The diagonal components of $\underset{\sim}{S}$ are linearly dependent, that is, the trace can assume any value and still give rise to the same calculated U_{ij}'s. Thus, a singularity should occur in the inversion of the least-squares normal-equation matrix. One way in which this singularity can be avoided is by constraining the trace of $\underset{\sim}{S}$ to be zero.

TFPA is clearly not a rigid molecule, but it does have rigid segments. The principal interest in thermal motion in this work was in connection with correction of intra-molecular distance and angle parameters. Separate analyses of the thermal parameters of the three segments N—⟨◯⟩—F were made, which were sufficient to furnish corrections for all bond lengths and angles except the angles at the nitro-gen atom. The method used was that of Schomaker and Trueblood (21) as embodied in a computer program of C. K. Johnson. The constraint that the trace of $\underline{S}$ be zero was applied. The values of the standard deviations of an observation of unit weight[*], σ_{uw}, for the three segments including ring 1, ring 2, and ring 3, respectively, are 0.0027, 0.0030, and 0.0024 $\overset{o}{A}{}^2$. The values indicate that the fit to the rigid-body model is fairly good for each segment. Rigid-body calculations based upon the individual segments N—⟨◯⟩ and ⟨◯⟩—F were performed without significant improvement in the fit over that of the first model.

The detailed description of the rigid-body motions resulting from the analyses of the three segments are given

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*This quantity σ_{uw} is defined by

$$\sigma_{uw} \equiv \sum w(U^o_{ij,r} - U^c_{ij,r})^2/(n-p),$$

where the number of observations n is six times the number of atoms in the segment and the number of parameters P determined is twenty. Unit weights w were used.

in Table IX. Included for each segment is the description
preferred by Schomaker and Trueblood (21), in terms of
three independent screw librations (helical motions) about
nonintersecting axes and three reduced translations. The
screw pitch σ_i given in the table for each principal axis
of libration is defined as

$$\sigma_i = \frac{S_{ii}}{L_{ii}}$$

The Cartesian unit base vectors have been defined for
each segment such that $\underline{i}_1$ has the direction of the vector
C(4) to C(1); $\underline{i}_2$ has the direction of this vector crossed
into the vector from C(5) to C(3); and $\underline{i}_3$ completes the
right-handed Cartesian set. Note that for rings 2 and 3
the axes of maximum vibration are very close to the
C(1)-C(4) axes, as one might expect. The axis of maximum
vibration in ring 1 has no such simple relation to the
Cartesian base vectors.

The libration tensors from the analyses were used to
calculate the corrections to bond lengths and angles
(15, 21). The results are discussed below under the head-
ing of Molecular and Crystal Structures.

The root-mean-square vibrational amplitudes for each
atom of TIPA in the three principal axis directions are
given in Table X. The iodine atom of ring 2 of molecule 2
has the unusually large root-mean-square displacement of
0.643 $\overset{o}{A}{}^2$. No segmented-body thermal-motion analysis of

TABLE IX

DESCRIPTION OF THE MOTIONS OF THE RIGID SEGMENTS
OF THE TRI-(p-FLUOROPHENYL)-AMINE MOLECULE

	Ring 1			
	Crystal Coordinates			Cartesian Coordinates ($\overset{o}{A}$)		
	x	y	z	X	Y	Z
Reaction center	0.36385	0.07270	0.74558	-0.0056	-0.0020	-0.0163

	Tensor Elements x 10^5					
Tensor	11	22	33	12	13	23
$\underline{L}$(rad.^{2})	1123(190)	833(46)	508(30)	146(80)	-123(101)	-324(31)
$\underline{T}$($\overset{o}{A}{}^2$)	5244(98)	4890(129)	4137(236)	-460(102)	441(128)	780(124)
$\underline{S}$(rad. x $\overset{o}{A}$)	113(78)	91(60)	-205(50)	39(110)	28(70)	322(44)

		Helical Axis K or principal axis K		
		1	2	3
Helical motions about nonintersecting axes				
R.M.S. amplitude				
(Radians)		0.1128	0.0941	0.0555
(Degrees)		6.4629	5.3896	3.1780
Pitch ($\overset{o}{A}$/radians)		-0.022	-0.152	0.526
Orientation angles of helical axes to Cartesian base vectors	$\underline{i}_1$	38.2	128.1	87.9
	$\underline{i}_2$	59.0	46.8	58.9
	$\underline{i}_3$	110.1	112.8	31.2
Displacement ($\overset{o}{A}$) of each helical axis K from other two helical axes J	J = 1	0.0	0.220	-0.634
	2	-0.166	0.0	0.687
	3	-0.142	0.204	0.0
Reduced translations				
R.M.S. amplitude ($\overset{o}{A}$)		0.235	0.227	0.179
Orientation angles of principal axes to Cartesian base vectors	$\underline{i}_1$	30.4	113.5	71.7
	$\underline{i}_2$	120.4	129.1	54.0
	$\underline{i}_3$	92.1	131.7	138.2

TABLE IX--Continued

Ring 2

	Crystal Coordinates			Cartesian Coordinates (Å)		
	x	y	z	X	Y	Z
Reaction center	0.67173	0.12284	0.91254	0.0033	-0.0029	-0.0094

Tensor	Tensor Elements x 10^5					
	11	22	33	12	13	23
$\underline{L}$(rad.^{2})	1706(212)	518(51)	918(34)	63(89)	7(113)	-195(35)
$\underline{T}$(Å^2)	3726(107)	6460(135)	4747(252)	-454(114)	-49(147)	411(136)
$\underline{S}$(rad. x Å)	29(85)	143(68)	-172(58)	-51(129)	8(84)	1(53)

		Helical Axis K or Principal Axis K		
		1	2	3
Helical motions about nonintersecting axes				
R.M.S. amplitude				
(Radians)		0.1307	0.0999	0.0660
(Degrees)		7.4900	5.7219	3.809
Pitch (Å/radians)		0.14	-0.128	0.238
Orientation angles of helical axes to Cartesian base vectors	$\underline{i}_1$	3.1	88.6	87.2
	$\underline{i}_2$	86.9	112.0	157.8
	$\underline{i}_3$	90.3	22.0	112.0
Displacement (Å) of each helical axis K from other two helical axes J	J = 1	0.0	0.110	-0.253
	2	-0.020	0.0	0.077
	3	0.014	-0.024	0.0
Reduced translations				
R.M.S. amplitude (Å)		0.257	0.215	0.191
Orientation angles of principal axes to Cartesian base vectors	$\underline{i}_1$	81.3	92.9	9.2
	$\underline{i}_2$	164.4	77.5	80.8
	$\underline{i}_3$	102.8	167.1	90.9

TABLE IX--Continued

Ring 3

	Crystal Coordinates			Cartesian Coordinates ($\overset{o}{A}$)		
	x	y	z	X	Y	Z
Reaction center	0.44053	0.16137	1.08985	-0.0061	-0.0133	0.0243

Tensor Elements x 10^5

Tensor	11	22	33	12	13	23
$\underline{L}$(rad.^{2})	1872(173)	724(42)	507(28)	-163(73)	94(92)	-293(28)
$\underline{T}$($\overset{o}{A}{}^2$)	5039(90)	5146(115)	4975(205)	903(94)	-586(119)	503(116)
$\underline{S}$(rad. x $\overset{o}{A}$)	65(73)	169(56)	-233(51)	-119(105)	236(73)	424(45)

		Helical Axis K or Principal Axis K		
		1	2	3
Helical motions about nonintersecting axes				
R.M.S. amplitude				
(Radians)		0.1382	0.0944	0.0550
(Degrees)		7.9154	5.4110	3.1511
Pitch ($\overset{o}{A}$/radians)		0.070	-0.487	0.993
Orientations angles of helical axes to Cartesian base vectors	$\underline{i}_1$	10.8	79.2	89.4
	$\underline{i}_2$	99.2	36.5	55.0
	$\underline{i}_3$	84.3	124.4	35.0
Displacement ($\overset{o}{A}$) of each helical axis K from other two helical axes J	J = 1	0.0	0.391	-1.153
	2	-0.020	0.0	0.124
	3	-0.077	0.166	0.0
Reduced translations				
R.M.S. amplitude ($\overset{o}{A}$)		0.237	0.231	0.191
Orientation angles of principal axes to Cartesian base vectors	$\underline{i}_1$	38.3	104.8	55.6
	$\underline{i}_2$	52.1	64.4	131.2
	$\underline{i}_3$	94.4	30.1	60.3

TABLE X

ROOT-MEAN-SQUARE AMPLITDUES (Å) OF VIBRATION IN THE PRINCIPAL-
AXIS DIRECTIONS FOR THE CARBON, NITROGEN, AND IODINE ATOMS
IN THE TRI-(p-IODOPHENYL)-AMINE STRUCTURE

Molecule 1

Atoms	Ring 1			Ring 2			Ring 3		
	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3
N	0.19(2)	0.23(2)	0.25(2)						
C(1)	.17(2)	.21(2)	.25(2)	0.19(2)	0.22(2)	0.25(2)	0.14(3)	0.21(2)	0.27(2)
C(2)	.17(3)	.22(2)	.29(2)	.17(3)	.26(2)	.29(2)	.18(2)	.22(2)	.25(2)
C(3)	.20(3)	.25(2)	.28(2)	.21(2)	.24(2)	.29(2)	.18(3)	.23(2)	.24(2)
C(4)	.14(3)	.21(2)	.29(2)	.17(2)	.22(2)	.27(2)	.17(2)	.20(2)	.25(2)
C(5)	.19(2)	.24(2)	.26(2)	.17(2)	.24(2)	.26(2)	.20(2)	.22(2)	.28(2)
C(6)	.18(2)	.22(2)	.25(2)	.16(2)	.24(2)	.27(2)	.18(2)	.23(2)	.26(2)
I	.197(2)	.290(2)	.375(2)	.195(2)	.292(2)	.337(2)	.206(2)	.280(2)	.312(2)

TABLE X--Continued

Molecule 2

Atoms	Ring 1			Ring 2			Ring 3		
	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3	Axis 1	Axis 2	Axis 3
N	0.17(2)	0.21(2)	0.30(2)	0.15(3)	0.20(2)	0.22(2)	0.17(2)	0.18(2)	0.28(2)
C(1)	.19(2)	.22(2)	.26(2)	.13(3)	.23(2)	.24(2)	.18(3)	.21(2)	.29(2)
C(2)	.19(2)	.21(2)	.28(2)	.22(2)	.23(2)	.27(2)	.15(3)	.26(2)	.29(2)
C(3)	.20(2)	.24(2)	.28(2)	.18(3)	.23(2)	.35(2)	.18(3)	.21(2)	.32(2)
C(4)	.17(3)	.21(2)	.31(2)	.17(3)	.25(2)	.30(2)	.20(3)	.25(2)	.31(2)
C(5)	.17(3)	.23(2)	.28(2)	.20(2)	.21(2)	.28(2)	.18(2)	.25(2)	.29(2)
C(6)	.17(3)	.21(2)	.26(2)						
I	.202(2)	.276(2)	.479(2)	.209(2)	.285(2)	.643(2)	.204(2)	.238(2)	.422(2)

TIPA was attempted, because the thermal parameters of the light atoms were not sufficiently well determined because of the presence of the iodine atoms.

Molecular and Crystal Structures

Figure 3 shows a stereoscopic view of the TFPA molecule in the direction normal to the plane of the three carbon atoms attached to the central nitrogen atom; Figure 3 also shows similar views of the two molecules of TIPA. Values of the valence angles at the nitrogen atoms and of the bond lengths C-N, C-C, C-F, and C-I are included in the molecular drawings. Table XI gives all bond lengths and angles for TFPA; when a second value is included for a length or angle, it is the corrected value obtained by use of the $\underline{L}$ tensor from the thermal-motion analysis. The bond-length corrections range from 0.0083 $\overset{o}{A}$ to 0.0164 $\overset{o}{A}$, the average correction being 0.0115 $\overset{o}{A}$, which is approximately six times the average standard error of the uncorrected lengths. The angle corrections ranged from 0.02^{o} to 0.29^{o}, the average correction being 0.14^{o}, which is approximately one standard error of an uncorrected angle. These corrections should be reliable, since the fit to the rigid-body model was good.

Table XII gives all the bond lengths and angles for molecules 1 and 2 of TIPA.
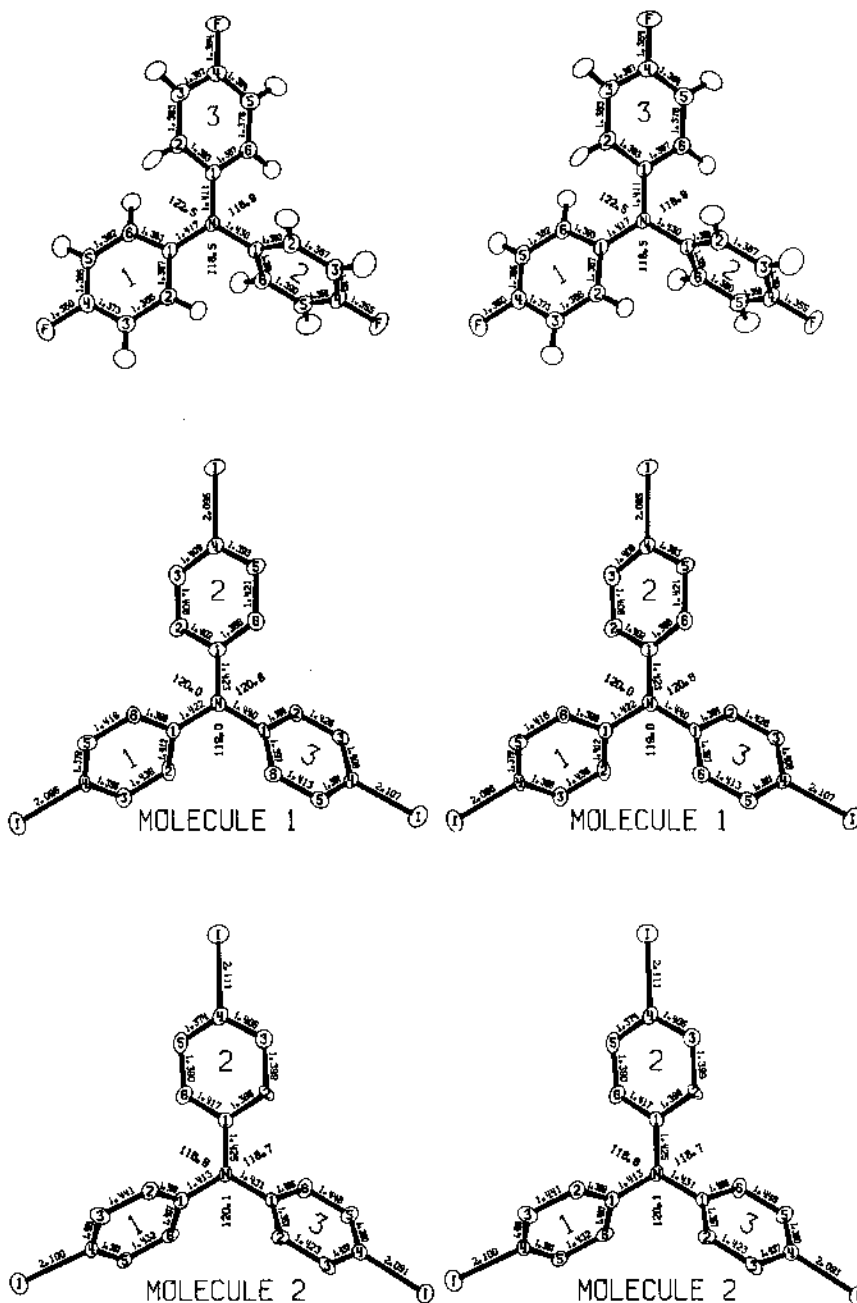
Fig. 3--Stereoscopic views of the molecules of tri-(*p*-fluorophenyl)-amine and of the two different molecules of tri-(*p*-iodophenyl)-amine. Drawings are all to the same scale, and the view direction in each case is normal to the plane of the three carbons attached to nitrogen.

TABLE XI

BOND LENGTHS (Å) AND VALENCE ANGLES (DEGREES)
IN TRI-(p-FLUOROPHENYL)-AMINE (SEE TEXT
FOR FURTHER EXPLANATION

Atoms	Ring I		
	I=1	I=2	I=3
N—C(1)	1.4167(14)	1.4305(12)	1.4109(14)
	1.426	1.441	1.420
C(1)—C(2)	1.3875(16)	1.3797(18)	1.3934(15)
	1.399	1.396	1.407
C(2)—C(3)	1.3857(18)	1.3872(18)	1.3826(19)
	1.395	1.397	1.391
C(3)—C(4)	1.3727(20)	1.3616(22)	1.3672(22)
	1.383	1.377	1.383
C(4)—C(5)	1.3653(20)	1.3586(22)	1.3636(22)
	1.377	1.375	1.377
C(5)—C(6)	1.3820(18)	1.3897(17)	1.3777(20)
	1.391	1.400	1.386
C(6)—C(1)	1.3934(15)	1.3790(17)	1.3866(17)
	1.403	1.395	1.402
C(4)—F	1.3600(14)	1.3554(14)	1.3637(14)
	1.369	1.365	1.372
C(2)—H(2)	0.994(12)	0.971(14)	0.965(14)
C(3)—H(3)	0.997(16)	1.015(19)	0.953(13)
C(5)—H(5)	0.972(15)	0.993(14)	0.997(17)
C(6)—H(6)	0.987(12)	0.965(14)	0.992(14)
C(1,J)—N—C(1,K)	118.87(09)	122.49(09)	118.51(09)
J,K ≠ I			

TABLE XI--<u>Continued</u>

Atoms	Ring I		
	I=1	I=2	I=3
N—C(1)—C(2)	120.04(10)	120.25(11)	121.89(11)
	120.06	120.13	121.68
N—C(1)—C(6)	121.18(11)	119.74(12)	119.47(10)
	121.08	119.57	119.39
C(2)—C(1)—C(6)	118.78(11)	120.01(11)	118.64(12)
	118.86	120.30	118.93
C(1)—C(2)—C(3)	120.98(12)	120.08(14)	120.59(13)
	121.00	119.97	120.38
C(2)—C(3)—C(4)	118.36(13)	118.43(14)	118.74(13)
	118.22	118.26	118.68
C(3)—C(4)—C(5)	122.42(12)	122.99(12)	122.20(13)
	122.49	123.27	122.47
C(4)—C(5)—C(6)	119.01(12)	118.53(14)	119.06(15)
	119.04	118.42	118.85
C(5)—C(6)—C(1)	120.48(13)	119.95(14)	120.75(14)
	120.38	119.78	120.68
C(3)—C(4)—F	118.75(13)	118.50(15)	118.59(13)
	118.66	118.33	118.53
C(5)—C(4)—F	118.83(13)	118.52(14)	119.21(15)
	118.85	118.40	119.00
C(1)—C(2)—H(2)	119.8(7)	119.3(9)	120.0(8)
C(3)—C(2)—H(2)	119.2(7)	120.6(9)	119.4(8)
C(2)—C(3)—H(3)	120.2(1.0)	120.7(1.1)	122.6(1.0)
C(4)—C(3)—H(3)	121.5(1.0)	120.8(1.1)	118.7(1.0)
C(4)—C(5)—H(5)	119.6(9)	119.6(1.0)	120.8(1.1)
C(6)—C(5)—H(5)	121.4(9)	121.8(1.0)	120.0(1.1)
C(5)—C(6)—H(6)	120.9(8)	121.6(9)	120.3(8)
C(1)—C(6)—H(6)	118.6(8)	118.5(9)	118.9(8)

TABLE XII

BOND LENGTHS ($\overset{\text{O}}{\text{A}}$) AND VALENCE ANGLES (DEGREES)
IN TRI-(p-IODOPHENYL)-AMINE

Molecule 1

	Ring I		
Atoms	I=1	I=2	I=3
N-C(1)	1.422(15)	1.423(14)	1.440(14)
C(1)-C(2)	1.412(16)	1.402(16)	1.394(16)
C(2)-C(3)	1.436(16)	1.408(17)	1.426(16)
C(3)-C(4)	1.396(17)	1.409(16)	1.408(15)
C(4)-C(5)	1.379(16)	1.393(16)	1.391(16)
C(5)-C(6)	1.416(16)	1.421(16)	1.413(16)
C(6)-C(1)	1.399(16)	1.386(17)	1.397(16)
C(4)-I	2.096(12)	2.095(13)	2.107(12)
C(1,J)-N-C(1,K)	120.8(1.2)	119.0(1.2)	120.0(1.2)
J,K ≠ I			
N-C(1)-C(2)	119.4(1.3)	117.3(1.4)	117.3(1.3)
N-C(1)-C(6)	118.8(1.3)	119.7(1.4)	119.0(1.4)
C(2)-C(1)-C(6)	121.8(1.3)	123.0(1.4)	123.6(1.4)
C(1)-C(2)-C(3)	118.6(1.3)	117.3(1.4)	119.2(1.3)
C(2)-C(3)-C(4)	117.6(1.4)	119.8(1.4)	116.9(1.2)
C(3)-C(4)-C(5)	124.1(1.3)	122.5(1.4)	123.4(1.3)
C(4)-C(5)-C(6)	118.6(1.3)	117.3(1.4)	119.6(1.4)
C(5)-C(6)-C(1)	119.3(1.3)	119.9(1.4)	117.4(1.3)
C(3)-C(4)-I	117.7(1.1)	119.7(1.2)	117.5(1.0)
C(5)-C(4)-I	118.2(1.0)	117.7(1.1)	119.1(1.0)

TABLE XII--Continued

Molecule 2

Ring I

Atoms	I=1	I=2	I=3
N–C(1)	1.413(14)	1.425(14)	1.431(13)
C(1)–C(2)	1.390(16)	1.398(14)	1.367(16)
C(2)–C(3)	1.441(16)	1.399(16)	1.423(16)
C(3)–C(4)	1.401(17)	1.406(16)	1.437(17)
C(4)–C(5)	1.391(17)	1.374(18)	1.380(18)
C(5)–C(6)	1.432(16)	1.390(16)	1.448(17)
C(6)–C(1)	1.407(16)	1.417(15)	1.406(16)
C(4)–I	2.100(14)	2.111(15)	2.091(14)
C(1,J)–N–C(1,K)	118.7(1.1)	120.1(1.1)	118.8(1.1)
J,K ≠ I			
N–C(1)–C(2)	119.0(1.4)	121.3(1.2)	118.6(1.3)
N–C(1)–C(6)	117.1(1.3)	117.5(1.2)	117.9(1.3)
C(2)–C(1)–C(6)	123.9(1.4)	121.2(1.2)	123.5(1.3)
C(1)–C(2)–C(3)	119.5(1.4)	117.9(1.2)	119.0(1.3)
C(2)–C(3)–C(4)	115.2(1.4)	118.9(1.3)	117.7(1.3)
C(3)–C(4)–C(5)	126.2(1.4)	124.4(1.4)	123.8(1.4)
C(4)–C(5)–C(6)	117.7(1.4)	116.3(1.4)	116.8(1.4)
C(5)–C(6)–C(1)	117.3(1.3)	121.2(1.4)	119.2(1.4)
C(3)–C(4)–I	115.5(1.1)	116.3(1.2)	117.8(1.2)
C(5)–C(4)–I	118.3(1.2)	119.2(1.2)	118.4(1.2)

Figure 4 gives the averages of the corrected values of the chemically equivalent bond lengths and angles for TFPA and the corresponding averages of the uncorrected bond lengths and angles for TIPA, with root-mean-square deviations from the averages.

Table XIII gives the equations of the least-squares best planes (11, 20) through the atoms of the rings 1, 2, and 3 of TFPA, with the deviations of various atoms from these planes; Table XIV gives the corresponding data for the two molecules of TIPA. Figure 5 shows the same deviations from the best-planes for both TFPA and TIPA, but for nonhydrogen atoms only.

In TFPA the best planes through the carbon atoms of rings 1, 2, and 3 make angles with the plane defined by the three carbon atoms attached to nitrogen of 31.8^O, 59.1^O, and 30.6^O respectively. These are essentially the angles ϕ' as defined in Chapter I. In TIPA the corresponding angles are 43.4^O, 33.1^O, and 44.2^O in molecule 1 and 56.6^O, 27.3^O, and 52.3^O in molecule 2. These varied ring twists are obviously requirements for packing of the molecule into crystals.

It is clear from the values of the valence angles of the nitrogen atoms in Figure 3 that the valence configurations of nitrogen in the TFPA molecule and the two TIPA molecules are all nearly plane trigonal configurations. The nitrogen atom in TFPA is displaced from the plane of its three carbon neighbors by $0.029 \overset{O}{A}$. This displacement,
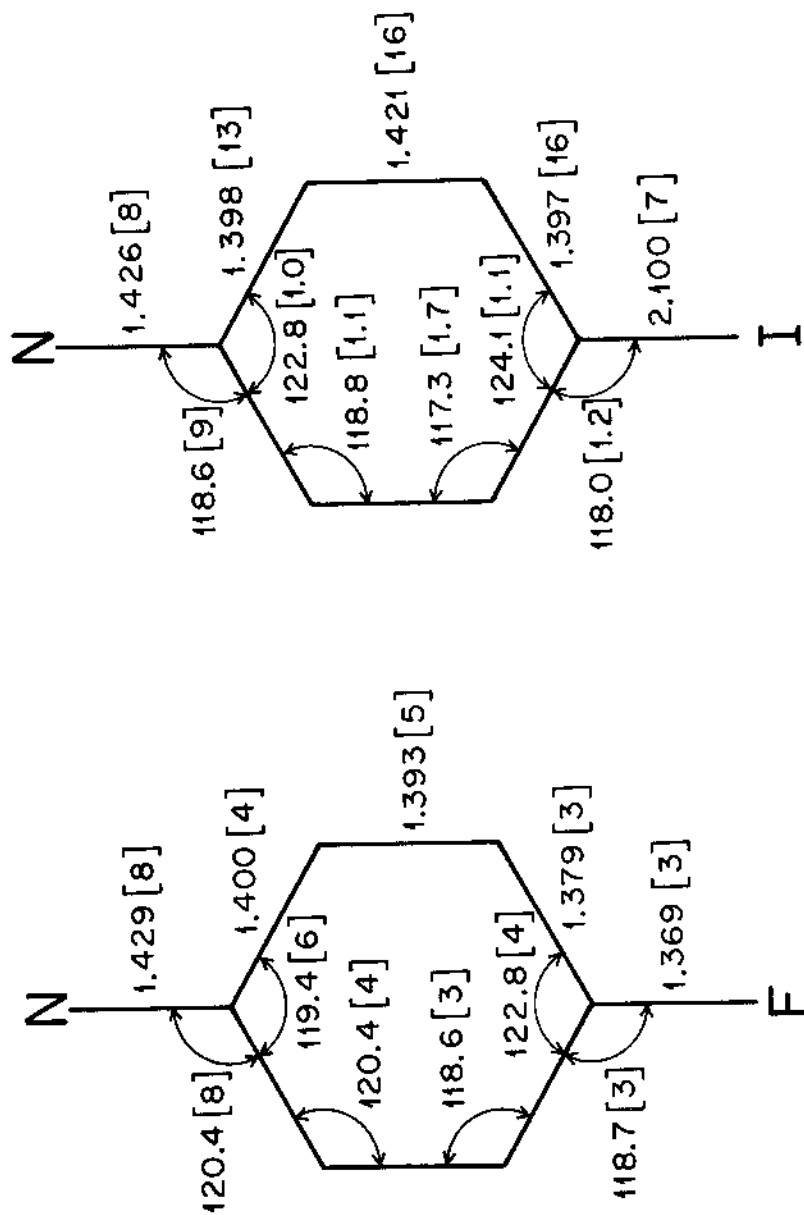
Fig. 4--Average bond lengths (Å) and angles (°) in tri-(*p*-fluorophenyl)-amine and tri-(*p*-iodophenyl)-amine, with root-mean-square deviations from averages.

TABLE XIII

EQUATIONS OF THE BEST LEAST-SQUARES PLANES THROUGH THE
THREE RINGS OF TRI-(p-FLUOROPHENYL)-AMINE AND DEVIA-
TIONS OF VARIOUS ATOMS FROM THE BEST PLANES

Equations of Best Planes

Ring 1 $4.5465X + 11.2944Y - 6.1872Z = 1.9648$ Å

Ring 2 $-.2355X - 14.4599Y - 4.3988Z = 6.0053$ Å

Ring 3 $-4.8686X + 11.7936Y - 3.3051Z = 4.0027$ Å

Distances of Atoms from Best Planes (Å)

Atoms	Ring 1	Ring 2	Ring 3
N	−0.0217(12)	0.0036(12)	0.0033(10)
C(1)	−0.0047(12)	−0.0009(12)	0.0053(11)
C(2)	−0.0024(13)	0.0017(14)	−0.0066(12)
C(3)	0.0058(16)	0.0003(17)	0.0008(14)
C(4)	−0.0020(15)	−0.0031(17)	0.0064(15)
C(5)	−0.0052(16)	0.0038(16)	−0.0075(16)
C(6)	0.0086(15)	−0.0018(14)	0.0016(14)
F	−0.0004(11)	−0.0058(12)	0.0299(10)
H(2)	−0.024(14)	−0.043(16)	−0.030(14)
H(3)	0.006(19)	−0.042(19)	0.021(14)
H(5)	−0.002(16)	−0.014(16)	−0.077(18)
H(6)	0.014(15)	−0.014(15)	−0.018(14)

TABLE XIV

EQUATIONS OF THE BEST LEAST-SQUARES PLANE THROUGH THE
THREE RINGS OF TRI-(p-IODOPHENYL)-AMINE AND DEVI-
ATIONS OF VARIOUS ATOMS FROM THE BEST PLANES

Molecule 1

Equations of Best Planes

Ring 1 $-23.6569X - 17.7716Y + 3.5439Z = 12.0626 \overset{o}{A}$

Ring 2 $-12.0234X - 19.7822Y - 6.9893Z = 10.8938 \overset{o}{A}$

Ring 3 $-41.0048X + 25.1807Y - 3.6688Z = 1.4339 \overset{o}{A}$

Distances of Atoms from Best Planes ($\overset{o}{A}$)

Atoms	Ring 1	Ring 2	Ring 3
N	-0.003(08)	-0.005(09)	0.030(12)
C(1)	0.006(10)	-0.003(10)	0.002(16)
C(2)	-0.004(10)	-0.020(11)	-0.005(14)
C(3)	0.000(10)	0.020(11)	0.004(14)
C(4)	0.001(10)	0.002(10)	-0.002(14)
C(5)	0.001(10)	-0.024(10)	0.000(16)
C(6)	-0.004(09)	0.025(10)	0.000(15)
I	0.011(02)	-0.050(01)	0.037(02)

TABLE XIV--<u>Continued</u>

<u>Molecule 2</u>

Equations of Best Planes

Ring 1	$-33.4169X + 17.0249Y - 6.6642Z = 1.8376$ Å
Ring 2	$-14.6733X - 28.2068Y - 1.8972Z = 18.8066$ Å
Ring 3	$27.1169X - 30.1661Y - 6.7177Z = 9.5694$ Å

Distances of Atoms from Best Planes (Å)

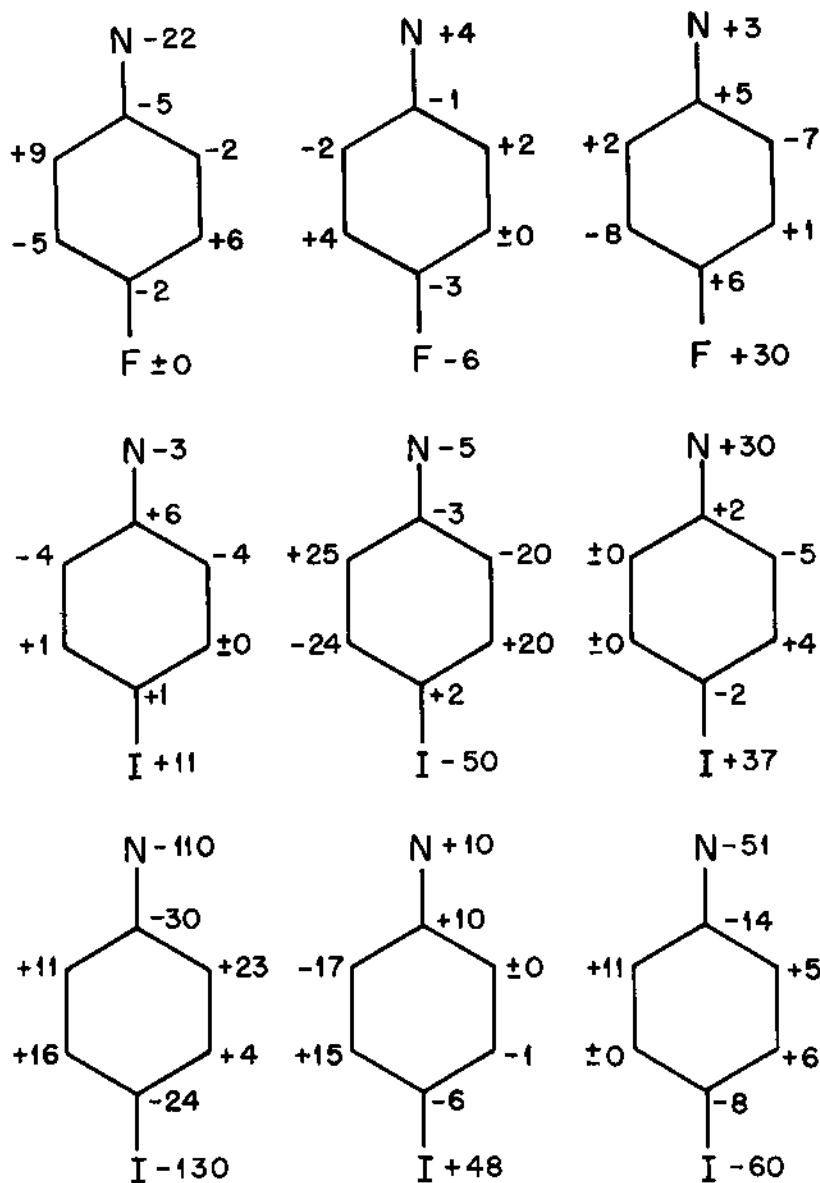| Atoms	Ring 1	Ring 2	Ring 3
N	-0.110(11)	0.010(08)	-0.051(12)
C(1)	-0.030(14)	0.010(09)	-0.014(14)
C(2)	0.023(13)	-0.000(09)	0.005(15)
C(3)	0.004(14)	-0.001(10)	0.006(15)
C(4)	-0.024(14)	-0.006(10)	-0.008(16)
C(5)	0.016(14)	0.015(10)	-0.000(16)
C(6)	0.011(14)	-0.017(10)	0.011(15)
I	-0.130(02)	0.048(02)	-0.060(02)

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Fig. 5--Deviations from best planes of ring atoms in tri-(*p*-fluorophenyl)-amine and in the two different molecules of tri-(*p*-iodophenyl)-amine (A$^\circ$, x 1000).

though about 24 times the standard error (σ) of position of the nitrogen atom along the plane normal, is still quite small; it corresponds to the bending of each C-N bond from a hypothetical plane configuration by only 1.2^O. In molecule 1 of TIPA the nitrogen atom is $0.027 \overset{O}{A}$ (~3σ) from the plane of the three carbons, and the C-N bond configuration is barely distinguishable from the plane configuration. In molecule 2 the nitrogen atom is $0.129 \overset{O}{A}$ (15σ) from the plane, corresponding to bending each C-N bond from a plane configuration by 4.8^O. For comparison, the C-N-C valence angle of 116° reported for triphenylamine (18) corresponds to a displacement of the nitrogen atom from the three-carbon plane of $0.29 \overset{O}{A}$ and a bending of each C-N bond of 11.7^O.

The fact that the TIPA crystal contains two molecules per asymmetric unit provides some data as to what degree of deformation of the nitrogen valence geometry in triphenylamines may be expected from packing effects. The relative distortion between molecules 1 and 2 in TIPA is more than the slight distortion in the TFPA molecule or that in molecule 1 of TIPA from the hypothetical plane configuration. The conclusion is that there is no significant inherent difference between the nitrogen atoms in TFPA and TIPA so far as valence geometry is concerned and that it is possible that molecules of both compounds in solution or in the gaseous state have the plane valence configuration at nitrogen.

In these same molecules there are some other small distortions that are to be attributed to packing. For example, in TFPA the fluorine atom on ring 3 is displaced from the least-squares best plane through the six carbon atoms by 0.030 Å (30σ), more than three times the displacement of any carbon atom from its best plane. Similarly, the nitrogen atom is 0.022 Å (19σ) from the best plane through ring 1. In TIPA the iodine atom on ring 1 of molecule 2 is displaced 0.130 Å (65σ) from the best plane. The largest of the displacements of the carbon atoms from the best plane is 0.03 Å (~2σ), and the indication is that the displacement of the iodine atom is real.

The hybridization of the nitrogen atoms must be very nearly the ideal sp^2 plane trigonal hybridization. Presumably the nearly plane configuration signifies some stabilization through π-orbital overlap between the nitrogen atoms and the adjacent carbon atoms, even though all the rings are twisted far from the orientations allowing maximum overlap. Since the π-orbital overlap integral is proportional to $\cos\phi'$, one may expect the exact hybridization and valence geometry to depend on packing in an indirect manner through effects on the twist angles, as well as by way of direct strains.

The average C-N bond lengths in TFPA (corrected) and TIPA (uncorrected) are 1.429[8] and 1.426[8] Å respectively. These averages are shorter than the value 1.472(8) Å

reported from a microwave study of trimethylamine (17).

The C-N-C angle found in the microwave study was $108.7(1.0)^\circ$, nearly the angle of a regular tetrahedron. The difference in the C-N bond length between trimethylamine and the tri-(p-halophenyl)-amines must be attributed in part to the difference in hybridization of the nitrogen and carbon atoms. The decrease in the C-N single-bond length accompanying a change of bond hybridization from sp^3-sp^3 to sp^2-sp^2 may be expected to be about the same as the decrease for a C-C single bond length, for which various authors have estimated from 0.02 to 0.06 $\overset{o}{A}$--see references (9, 22, 23). The range of these estimates reflects the inherent difficulty in trying to separate the effects of hybridization from those of π conjugation and of steric hindrance.

It is of some interest to consider the individual values of the three C-N bond lengths in TFPA in relation to the three twist angles. The corrected C-N bond length 1.439 $\overset{o}{A}$ associated with the largest twist angle of 59.1° is significantly greater than the two other C-N bond lengths, 1.422 and 1.426 $\overset{o}{A}$. The difference amounts to about nine times the standard deviation of the difference in one case and seven times the standard deviation in the other. The longer bond length is 0.015 $\overset{o}{A}$ greater than the average of the other two. From a curve published by Suzuki (23) which correlates the inter-ring C-C bond lengths in biphenyl derivatives with the twist angles about the C-C bond, one

would expect a lengthening of 0.02 $\overset{\text{o}}{\text{A}}$ in twisting from 31$^\text{o}$

to 59$^\text{o}$. The curve should be expected to apply reasonably

well for C-N bonds if shifted along the bond-length axis.

The agreement seems quite good in view of the scatter of

points about the Suzuki curve. The C-N distances in the

two molecules of TIPA have not been determined with suffi-

cient precision to show the effects of twist.

The average corrected C-F distance in TFPA, 1.369[3] $\overset{\text{o}}{\text{A}}$,

is close to the value 1.368(19) $\overset{\text{o}}{\text{A}}$ reported in o-fluoro-

benzoic acid from X-ray analysis (16). Distances of

1.34 $\overset{\text{o}}{\text{A}}$ and 1.3315 $\overset{\text{o}}{\text{A}}$ have been reported for fluorobenzene

from electron-diffraction (2) and microwave (1) studies

respectively. The average C-I distance in TIPA, 2.100[7] $\overset{\text{o}}{\text{A}}$,

is somewhat longer than the C-I distance of 2.064(8) $\overset{\text{o}}{\text{A}}$

determined in X-ray analysis of p-iodobenzonitrile (12). A

C-I distance of 2.08 $\overset{\text{o}}{\text{A}}$ is reported from a microwave study

of iodobenzene (12).

An interesting feature of TFPA is the fact that the

angles C(3)-C(4)-C(5) are the largest ring angles and that

the chemically equivalent distances C(4)-C(3) and C(4)-C(5)

are the shortest ring distances. (See Table XI and

Figure 4.) These facts may be explained, following argu-

ments of Walsh (24), as an effect of the substitution of

the highly electronegative fluorine atoms on the atoms C(4).

According to Walsh the substitution of a fluorine atom on

C(4) should increase the electronegativity of C(4) relative

to C(3) and C(5) and at the same time increase the s char-
acter of the valences of C(4) toward C(3) and C(5) and
increase the p character of the valence toward fluorine.
The result is that the valence orbitals toward C(3) and
C(5) become intermediate between sp^2 and sp orbitals, with
a corresponding increase in the C(3)-C(4)-C(5) angle and a
decrease in the C(4)-C(3) and C(4)-C(5) distances.

Unfortunately, there is no ready explanation for the
variations in ring bond lengths and angles in TIPA. In
this case, of course, the differences are smaller multiples
of the standard errors because of the lower precision of
the determination.

Table XV gives the van der Waals radii of hydrogen,
carbon, nitrogen, fluorine, and iodine as presented in an

TABLE XV

VAN DER WAALS RADII OF HYDROGEN, CARBON,
NITROGEN, FLUORINE, AND IODINE ATOMS

Element	Radii (Å)
H(benzene).	1.00
C(benzene).	1.77
N	1.55
F (aryl).	1.47
I (aryl).	2.07

article by Bondi (3), and Table XVI lists the shortest
intermolecular distances between atom pairs in TFPA and

TABLE XVI

SHORTEST INTERMOLECULAR DISTANCES IN $\overset{\text{o}}{\text{A}}$
BETWEEN PAIRS OF ATOMS IN TFPA AND TIPA

	TFPA					TIPA		
	H	C	N	F		C	N	I
H	2.57				C	3.37		
C	2.80	3.52			N	2.93	>5	
N	3.85	4.16	4.60		I	3.57	4.31	3.79
F	2.54	3.25	4.12	3.25				

TIPA. Figures 6 and 7 show the packing within the unit cells of TFPA and TIPA.

There are three instances in which the intermolecular distances separating iodine atoms are closer than the sum of their van der Waals radii. The iodine atom of ring 3 molecule 1 is 3.92 $\overset{\text{o}}{\text{A}}$ from another symmetry-related atom. This close intermolecular distance is an end-on van der Waals contact. The iodine atom of ring 3 molecule 2 (reference atom) is 3.79 $\overset{\text{o}}{\text{A}}$ from two symmetry-related iodine atoms. The C-I bond of the reference iodine atom forms nearly orthogonal angles with the C-I bonds of the two symmetry related iodine atoms. There are five other intermolecular distances between atom pairs shorter than the sum of their van der Waals radii. Four of these five short intermolecular distances are contacts between carbon and
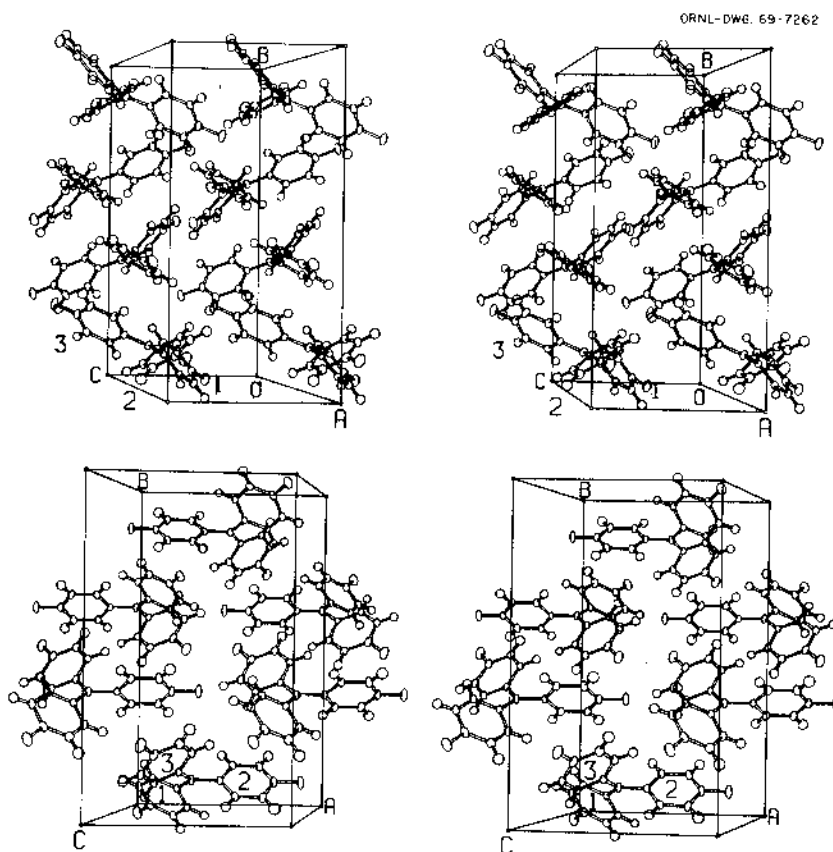
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Fig. 6—Stereoscopic views of the crystal structure of tri-(p-fluorophenyl)-amine along the directions -$\underset{\sim}{a}$* (Top) and -$\underset{\sim}{c}$* (Bottom).
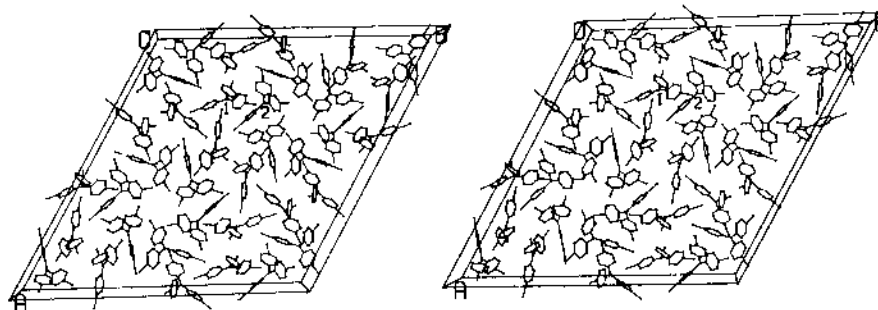
Fig. 7--Stereoscopic view of the crystal structure of tri-(p-iodophenyl)-amine in the direction - $\underset{\sim}{c}^*$.

iodine atoms; these contact distances range from 3.57 to 3.74 $\overset{\text{o}}{\text{A}}$. The remaining contact is between two carbon atoms and is listed in Table XVI.

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APPENDIX

The computer programs used in the various calculations
were as follows:

Least-squares determination of cell parameters--
Part of the program package for the Oak Ridge
computer-controlled diffractometer of Busing,
Ellison, Levy, King, and Roseberry (3).

Absorption corrections--Program modified by Ellison
and Levy (6) from Program OR ABS of Wehe, Busing,
and Levy (11).

Fourier syntheses--A version of the Program FORDAPER
of Zalkin (12) modified by Brunton (2).

Least-squares refinement of structure parameters--
Program XFLS modified by Johnson, Ellison, Levy,
and Yakel (10) from Program OR FLS of Busing,
Martin, and Levy (5).

Calculated positional parameters of hydrogen atoms--
Program HYCOR of Brown (1).

Bond lengths and angles--Program OR FFE-II by
Johnson (9), a modified version of Program OR FFE
by Busing, Martin, and Levy (4).

Rigid-body analysis--Program OR SBA of Johnson (9).
Least-squares best plane--Program BSPLAN of Hamilton
(7) modified by Brown (1).

Table of F_o's and F_c's--Program EDIT of Brown (1).

Drawings--Program OR TEP of Johnson (8).

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