Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Bart Kahr & Randall L. Carter (1992): Structures for Polymorphs of Triphenylchloromethane. Triphenylacetic Acid Illustrates the Isomorphous Stable Modification, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 219:1, 79-100

To link to this article: http://dx.doi.org/10.1080/10587259208032120

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 79–100
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Printed in the United States of America

STRUCTURES FOR POLYMORPHS OF TRIPHENYLCHLOROMETHANE. TRIPHENYLACETIC ACID ILLUSTRATES THE ISOMORPHOUS STABLE MODIFICATION.

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(Received February 28, 1992)

Triphenylacetic acid is isomorphous with the published structure of triphenylchloromethane (**I**). It crystallizes in the trigonal system, space group $P\bar{3}$, with a=b=14.105(3)Å, c=13.121(2)Å, V=2261(1)Å^3, Z=6 at 175K. The structure was solved by direct methods and refined to $R(F_o)$=0.062. We determined the structures for two triclinic polymorphs of triphenylchloromethane, **II** and **III**. The three forms were obtained from pentane evaporated at room temperature. Phases **I** and **III** were isolated from particular solvent systems. Crystal data (**II**): triclinic system, space group $P\bar{1}$, with a=13.028(1)Å, b=13.559(2)Å, c=13.969(3)Å, α=117.67(1)°, β=92.67(1)°, γ=91.43(1)°, V=2179.9Å^3, Z=6 at 228K. The structure was solved by direct methods and refined to $R(F_o)$=0.045. Crystal data (**III**): triclinic system, space group $P\bar{1}$, with a=14.1562(4)Å, b=21.3190(7)Å, c=13.0654(5)Å, α=99.92(3)°, β=92.68(3)°, γ=106.15(2)°, V=3712(2)Å^3, Z=10 at 248K. The structure was solved by direct methods and refined to $R(F_o)$=0.064. A batch of crystals from pentane showed three peaks in the DSC thermogram at 99°C (**III**), 108°C (**II**), and 111°C (**I**). Phase **III** melts without being transformed to phase **II** or phase **I**. Phase **II** could not be isolated for calorimetric studies.

Keywords: Triphenylchloromethane, Polymorphism, Triphenylacetic Acid, Differential scanning calorimetry, X-ray structure determination

1. INTRODUCTION

Previously, we described chiral electron density distributions in atoms with crystallographic C_3 site symmetry.[1] Triphenylchloromethane (TPMCl) was among the molecules for which we desired high-quality electron density maps; its trigonal X-ray structure had been reported.[2] In attempting to reproduce this crystal we encountered, and struggled against, the ubiquity of polymorphism in molecular crystals.[3] In this paper we compare the structures of two new triclinic

modifications obtained during the course of growing a trigonal crystal. In so doing we add eight independent X-ray determinations of the molecular structure of TPMCl to the three already described. Phase transitions are evidenced by differential scanning calorimetry (DSC). In addition, we report the crystal and molecular structure of triphenylacetic acid (TPMCOOH) which is isomorphous with, and therefore illustrative of, the trigonal TPMCl phase.

Triphenylchloromethane crystallizes in the trigonal system, space group $P\bar{3}$ and is isomorphous with triphenylbromomethane[4] (TPMBr). The compounds associate pairwise (halogen-to-halogen and triphenylmethyl-to-triphenylmethyl) and linearly with all carbon-halogen bonds aligned with the C_3 and S_6 axes of the lattice. Heterochiral triphenylmethyl propellers are interdigitated.[5] The associations were described as dimeric because the halogen-halogen distances in each case were smaller than the sums of the van der Waals radii.[2,4] We have subsequently discovered that TPMCOOH[5] is isomorphous with TPMCl and TPMBr; it forms common carboxylic acid dimers, and the isomorphism is accomplished by virtue of a statistical disordering of the carboxyl groups that permits the dimers to have averaged S_6 site symmetry.

While attempting to prepare trigonal crystals of TPMCl we grew a triclinic modification, $P\bar{1}$, Z=10. This crystal was indexed earlier by Gerdil and Dunand.[6,7] The solution of this structure showed that the TPMCl molecules also were aligned pairwise with close Cl·····Cl interactions, however the C-Cl bonds were no longer parallel. The structure could be succinctly described as a "jumbled" version of the trigonal modification. We surmised that the triclinic form was a kinetically stable structure that could be transformed thermally into the previously described trigonal phase. However, we were surprised to find *two* peaks in the thermogram of a batch of crystals, prior to melting of the trigonal phase, by DSC. A shoulder on the main transition corresponding to fusion was noted by Gerdil and Dunand[6] and they speculated that a third polymorph may exist within a few degrees of melting. By increasing the crystallization rate we enriched the elusive intermediate phase (**II**) in order to obtain a single crystal for X-ray diffraction studies. It also crystallizes in the triclinic system, $P\bar{1}$, Z=6. Its structure can be digested readily as a "gently jumbled" version of the trigonal phase. Its occurrence as an independent phase is surprising given the structural similitude with form **I**.

2. CRYSTALLOGRAPHY

2.1 Triphenylacetic acid

The space group $P\bar{3}$ has two independent threefold axes. Linear dimers of TPMCl and TPMBr are aligned along these axes in the isomorphous crystals (TPMCl: a=13.998(2)Å, c=13.202(4)Å; TPMBr: a=13.993(3)Å, c=13.438(4)Å). Crystals of TPMCOOH grown from chloroform indexed in the trigonal[8] system (a=14.705(3)Å, c=13.121(3)Å), and the structure[9] proved to be isomorphous with TPMBr and TPMCl. The three crystal structures each have one-third of each of three independent molecules in the asymmetric unit. One molecule is related by the S_6 axis (Wyckoff *a*) to its enantiomer. The other two molecules in each structure lie along the C_3 (Wyckoff *c*) axis. They form a dimer of approximate S_6 symmetry. Figure 1 shows the labeling scheme for the asymmetric unit of TPMCOOH as well as representations of C_3 and S_6 dimers. Table I summarizes the crystallographic data.

Table II lists salient molecular parameters for TPMCOOH. There is little structural variation among the three independent molecules and the dimers are similarly disposed to one another as measured by $C_{carboxyl}$-$C_{carboxyl}$ distances. Carboxylic acid dimers of TPMCOOH are to be expected. They have averaged trigonal symmetry with the methyl and carboxyl carbons lying on the threefold axes. The carboxyl groups are necessarily disordered about these axes.

On the other hand, the molecular symmetry of the halide dimers of TPMCl and TPMBr are compatible with the crystal symmetry in an ordered structure. These dimers are characterized by short X·····X contacts particularly in the case of TPMBr. Landais first observed short Br·····Br contacts in TPMBr in 1935.[10] Dunand and Gerdil's 1984 study supported this claim with increased sophistication.[2] Wyckoff *a* relates enantiotopic Br atoms at a length of 3.496(2)Å and the Br·····Br distance along Wyckoff *c* is 3.203(2)Å. These distances are shorter than the sum of the van der Waals radii of 3.70(Å). This study suggests that the X·····X associations in TPMCl and TPMBr may be an organizing principle in their solid states.

2.2 Triphenylchloromethane

Single crystals of phases **II** and **III** of TPMCl used in diffraction studies were obtained by evaporation of pentane solutions containing 0.5% acetyl chloride. The crystals of phase **II** were grown at a faster rate, however. Our indexing of **II** and

III was fortuitous as both forms were deposited under these conditions and they were not easily distinguished by morphology.

TABLE I

Crystallographic Data

Compound	TPMCOOH	TPMCl (I) From Ref.1	TPMCl (II)	TPMCl (III)
Formula	$C_{20}H_{16}O_2$	$C_{19}H_{15}Cl$	$C_{19}H_{15}Cl$	$C_{19}H_{15}Cl$
MW	288.3	278.8	278.8	278.8
Temperature, K	175	298	228	248
Radiation, Å	CuKα	MoKα	MoKα	CuKα
Crystal Size, mm	.51x.36x.29	.60x.40x.40	.31x.19x.17	.35x.35x.08
Crystal System	trigonal	trigonal	triclinic	triclinic
Space Group	$P\bar{3}$	$P\bar{3}$	$P\bar{1}$	$P\bar{1}$
Lattice Constants:				
a, Å	14.105(3)	13.998(2)	13.028(1)	14.1562(4)
b, Å	= *a*	= *a*	13.559(2)	21.3190(7)
c, Å	13.121(3)	13.202(2)	13.969(3)	13.0654(5)
α, deg	90	90	117.67(1)	99.92(3)
β, deg	90	90	92.67(1)	92.68(3)
γ, deg	120	120	91.431(8)	106.15(2)
V, Å^3	2261(1)	2240(1)	2179(1)	3712(2)
Z	6	6	6	10
d_{calcd}, g·cm^{-3}	1.27	1.24	1.27	1.25
μ_{calcd}, cm^{-1}	6.5	2.25	2.47	17.32
Diffractometer	Nicolet R3m	Philips PW1100	Enraf CAD4	Rigaku AFC5
2θ range, deg	3.00-110.00	*	4.00-50.00	3.00-80.00
Unique Data	2864	1380	7667	3751
Obsd Data	2569	905	4828	2737
Absorption Corr.	Psi-scans	none	Psi-scans	Psi-scans
$R(F_O)$, $R_W(F_O)$	0.062, 0.074	0.034, 0.025	0.045, 0.058	0.064, 0.084
Parameters	135	81	536	426
Residual e·Å^{-3}	0.3	*	0.2	0.4

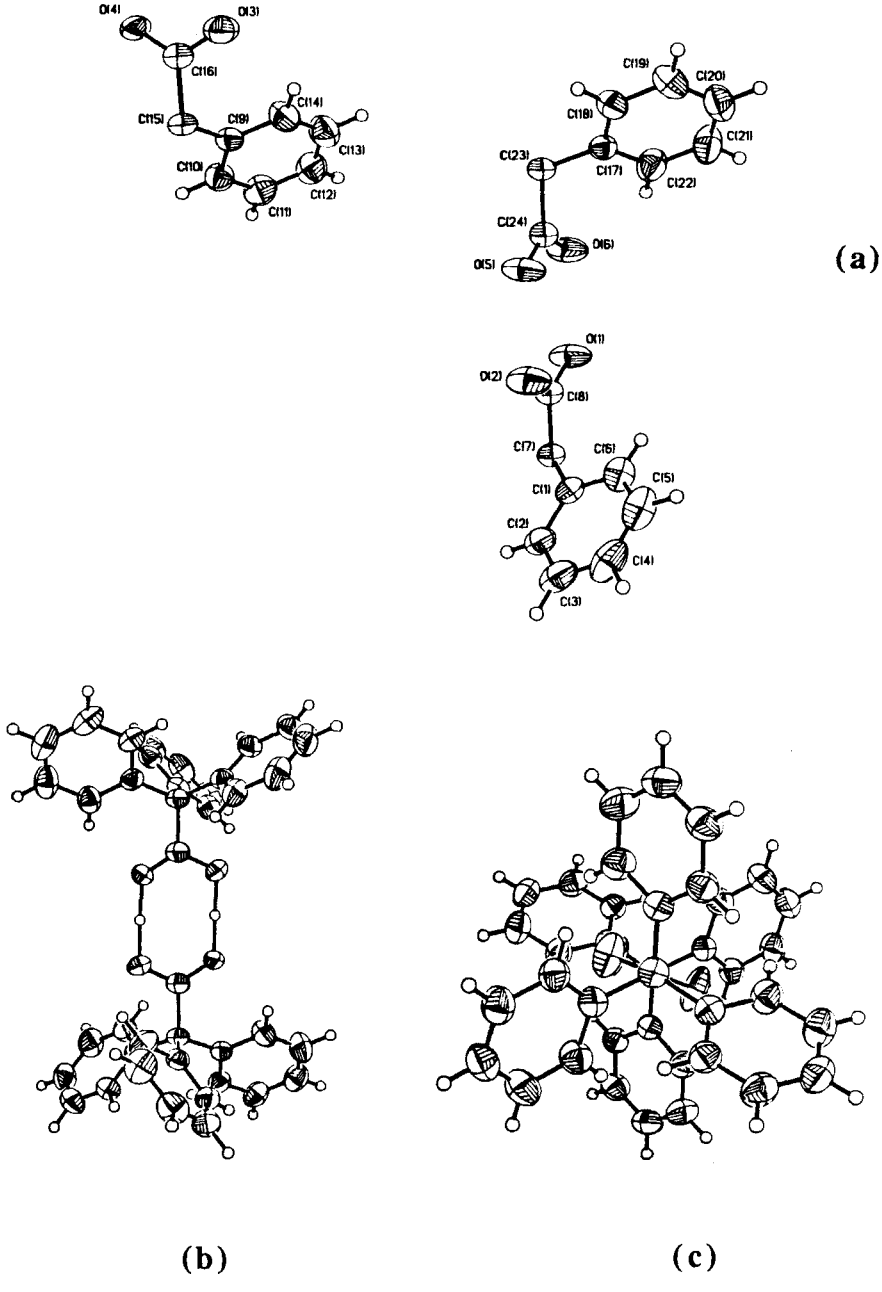

FIGURE 1. ORTEP representations (50% probability ellipsoids) of triphenylacetic acid (TPMCOOH). (a) Asymmetric unit with labeling scheme. Views of C_3 dimer (b) normal to the unique axis and of dimer along the S_6 axis (c). Only one carboxyl orientation is shown in each case.

TABLE II

Selected Molecular Parameters for TPMCOOH

Parameter	Length (Å)	Parameter	Angle (deg)
C(1)-C(7)	1.542(2)	C(1)-C(7)-C(8)	108.0(1)
C(9)-C(15)	1.546(1)	C(9)-C(15)-C(16)	108.4(1)
C(17)-C(23)	1.550(1)	C(17)-C(23)-C(24)	108.3(1)
C(7)-C(8)	1.547(3)	C(7)-C(8)-O(1)	122.4(2)
C(15)-C(16)	1.550(3)	C(7)-C(8)-O(2)	114.9(2)
C(23)-C(24)	1.546(3)	C(15)-C(16)-O(4)	122.5(3)
C(8)-O(1)	1.242(4)	C(15)-C(16)-O(3)	115.9(3)
C(8)-O(2)	1.253(2)	C(23)-C(24)-O(5)	122.0(5)
C(16)-O(3)	1.26(1)	C(23)-C(24)-O(6)	115.2(4)
C(16)-O(4)	1.24(1)	O(1)-C(8)-O(2)	122.3(3)
C(24)-O(5)	1.25(2)	O(3)-C(16)-O(4)	121.5(4)
C(24)-O(6)	1.25(2)	O(5)-C(24)-O(6)	122.7(6)
C(8).....C(24)	3.785(3)	C(1)-C(7)-C(1')[a]	110.9(1)
C(16).....C(16')	3.859(3)	C(9)-C(15)-C(9')	110.5(1)
		C(17)-C(23)-C(17')	110.6(1)

[a]Prime denotes symmetry related atom.

TABLE III

Atomic Positional and Isotropic Thermal Parameters for TPMCOOH

Atom	x	y	z	B(Å)^2
C(1)	0.7602(1)	0.3149(1)	0.9378(1)	3.4(1)
C(2)	0.8331(1)	0.3795(1)	1.0132(1)	4.0(1)
C(3)	0.9151(1)	0.3604(2)	1.0465(1)	5.2(1)
C(4)	0.9267(2)	0.2771(2)	1.0056(2)	5.7(1)
C(5)	0.8552(2)	0.2123(2)	0.9315(2)	5.4(1)
C(6)	0.7722(1)	0.2298(1)	0.8977(1)	4.3(1)
C(7)	2/3	1/3	0.9016(2)	3.2(1)
C(8)	2/3	1/3	0.7838(2)	3.5(1)
C(9)	-0.1176(1)	-0.0808(1)	0.3025(1)	3.2(1)
C(10)	-0.1684(1)	-0.0516(1)	0.3761(1)	3.9(1)
C(11)	-0.2720(1)	-0.1278(2)	0.4123(1)	4.7(1)
C(12)	-0.3253(1)	-0.2331(2)	0.3760(1)	4.9(1)
C(13)	-0.2759(1)	-0.2633(2)	0.3028(2)	5.2(1)
C(14)	-0.1730(1)	-0.1879(1)	0.2667(1)	4.5(1)
C(15)	0	0	0.2651(2)	3.2(1)
C(16)	0	0	0.1471(2)	3.5(1)
C(17)	0.7783(1)	0.4275(1)	0.3405(1)	3.2(1)
C(18)	0.7853(1)	0.4960(1)	0.2615(1)	3.9(1)
C(19)	0.8861(1)	0.5771(1)	0.2262(1)	4.7(1)
C(20)	0.9815(2)	0.5920(1)	0.2683(2)	5.1(1)
C(21)	0.9757(2)	0.5231(2)	0.3455(2)	5.5(1)
C(22)	0.8759(1)	0.4417(1)	0.3808(1)	4.6(1)
C(23)	2/3	1/3	0.3775(2)	3.1(1)

Atom	x	y	z	B(Å)^2
C(24)	2/3	1/3	0.4953(2)	3.4(1)
O(1)	0.5817(3)	0.2803(9)	0.7331(3)	5.2(3)
O(2)	0.621(1)	0.2403(3)	0.7436(3)	5.6(4)
O(3)	-0.008(1)	-0.0844(6)	0.1051(3)	5.6(4)
O(4)	0.008(1)	0.0773(6)	0.0965(2)	5.2(3)
O(5)	0.618(1)	0.371(1)	0.5458(2)	5.1(3)
O(6)	0.7203(9)	0.295(1)	0.5358(3)	5.1(3)

TABLE IV

Anisotropic Thermal Parameters for TPMCOOH

Atom	U11	U22	U33	U12	U13	U23
C(1)	0.046(1)	0.047(1)	0.037(1)	0.010(1)	0.006(1)	0.023(1)
C(2)	0.052(1)	0.055(1)	0.045(1)	0.010(1)	-0.002(1)	0.023(1)
C(3)	0.056(1)	0.073(1)	0.063(1)	0.023(1)	-0.006(1)	0.028(1)
C(4)	0.053(1)	0.075(1)	0.094(1)	0.035(1)	0.012(1)	0.036(1)
C(5)	0.058(1)	0.063(1)	0.091(1)	0.020(1)	0.021(1)	0.037(1)
C(6)	0.053(1)	0.053(1)	0.061(1)	0.006(1)	0.010(1)	0.030(1)
C(7)	0.047(1)	0.047(1)	0.031(1)	0	0	0.023(1)
C(8)	0.049(1)	0.049(1)	0.035(1)	0	0	0.025(1)
C(9)	0.044(1)	0.047(1)	0.033(1)	-0.001(1)	-0.005(1)	0.023(1)
C(10)	0.049(1)	0.053(1)	0.048(1)	-0.000(1)	0.003(1)	0.026(1)
C(11)	0.054(1)	0.069(1)	0.058(1)	0.006(1)	0.011(1)	0.031(1)
C(12)	0.047(1)	0.062(1)	0.066(1)	0.005(1)	-0.003(1)	0.018(1)
C(13)	0.058(1)	0.057(1)	0.067(1)	-0.009(1)	-0.005(1)	0.016(1)
C(14)	0.055(1)	0.056(1)	0.054(1)	-0.010(1)	-0.003(1)	0.023(1)
C(15)	0.047(1)	0.047(1)	0.026(1)	0	0	0.024(1)
C(16)	0.048(1)	0.048(1)	0.035(1)	0	0	0.024(1)
C(17)	0.044(1)	0.043(1)	0.035(1)	-0.005(1)	-0.001(1)	0.022(1)
C(18)	0.051(1)	0.054(1)	0.044(1)	0.007(1)	0.006(1)	0.029(1)
C(19)	0.062(1)	0.057(1)	0.059(1)	0.014(1)	0.016(1)	0.029(1)
C(20)	0.053(1)	0.052(1)	0.073(1)	0.002(1)	0.013(1)	0.018(1)
C(21)	0.045(1)	0.067(1)	0.086(1)	0.000(1)	-0.009(1)	0.018(1)
C(22)	0.051(1)	0.057(1)	0.059(1)	0.005(1)	-0.011(1)	0.021(1)
C(23)	0.045(1)	0.045(1)	0.029(1)	0	0	0.022(1)
C(24)	0.046(1)	0.046(1)	0.036(1)	0	0	0.023(1)
O(1)	0.038(1)	0.100(6)	0.034(2)	0.005(3)	-0.005(1)	0.014(3)
O(2)	0.111(6)	0.041(2)	0.040(2)	-0.009(2)	-0.005(3)	0.023(4)
O(3)	0.123(4)	0.065(4)	0.040(2)	-0.000(2)	0.003(3)	0.059(5)
O(4)	0.133(5)	0.046(3)	0.032(2)	0.004(2)	-0.001(3)	0.053(4)
O(5)	0.097(4)	0.114(5)	0.030(2)	0.003(3)	0.003(2)	0.089(3)
O(6)	0.095(5)	0.098(4)	0.034(2)	0.006(3)	-0.000(2)	0.072(3)

There is a one-to-one correspondence between the axes of trigonal **I** and triclinic **II** (Table I) with the unit cell of **II** being a slightly distorted version of the trigonal one. Cell parameters (**II**): triclinic system, space group $P\bar{1}$, with a=13.028(1)Å, b=13.559(2)Å, c=13.969(3)Å, α=117.67(1)°, β=92.67(1)°, γ=91.43(1)°, V=2179.9Å^3, Z=6 at 228K. The correspondence between **I** and **III**, described by Gerdil and Dunand[6], is accomplished by the application of a transformation matrix (1,0,0; 1/3,5/3,0; 0,0,1) to give a monoclinic cell which is then slightly distorted relative to the measured triclinic cell. Cell parameters (**III**): triclinic system, space group $P\bar{1}$, with a=14.1562(4)Å, b=21.3190(7)Å, c=13.0654(5)Å, α=99.92(3)°, β=92.68(3)°, γ=106.15(2)°, V=3712(2)Å^3, Z=10 at 248K.

The structures of **II** and **III** were solved by direct methods and refined using standard least-squares procedures. Tables V and VII list the atomic positional parameters for **II** and **III**, respectively, while Tables VI and VIII list the corresponding anisotropic thermal parameters.

Table IX summarizes salient molecular parameters for the three phases of TPMCl. We determined the geometries of 8 independent asymmetric TPMCl molecules in the two new triclinic structures adding to the 3 independent molecules in the trigonal (**I**) phase. Structural variations within the molecules are slight with C_{methyl}-Cl bond lengths varying between 1.840(3)Å and 1.874(6)Å. These bonds are longer than the standard C-Cl distances as previously noted by Dunand and Gerdil.[2] Valence angles C_{phenyl}-C_{methyl}-Cl varied between 105.5(2)° and 109.4(7)° among the 11 structures; they err on the short side of the tetrahedral value to accommodate the large phenyl groups, with concomitantly large C_{phenyl}-C_{methyl}-C_{phenyl} valence angles. Despite small geometric differences, all the TPMCl molecules in the triclinic structures adopt approximate C_3 symmetries with phenyl groups similarly twisted with respect to one another. A recent analysis showed that in most cases the conformations of crystallographically independent molecules are very similar.[11]

Similarities among the packing of **I**, **II**, and **III** are immediately obvious from inspection of views of the units cells shown in Figures 2 and 3. In each case the molecules align pairwise in an antiparallel fashion. The closest intermolecular Cl·····Cl and C_{methyl}·····C_{methyl} distances are nearly identical in structures **I**, **II**, and **III**. Deviations from strict linearity as in $P\bar{3}$ increase progressively from **I** to **III**. Table IX lists the largest angles between C_{methyl}-Cl vectors and vectors between translationally related Cl atoms. Whereas the molecules are constrained to be coparallel in **I**, the average deviations in **II** and **III** were 5.1° and 6.5°, respectively.

TABLE V

Atomic Positional and Isotropic Thermal Parameters for TPMCl (II)

Atom	x	y	z	B(Å)^2
Cl(1)	0.25273(6)	0.65180(7)	0.30642(7)	4.88(2)
Cl(2)	0.01635(6)	0.68210(7)	0.36862(6)	4.93(2)
Cl(3)	0.36550(6)	0.01645(7)	0.01058(7)	5.04(2)
C(1)	0.3952(2)	0.6614(2)	0.3185(2)	3.30(7)
C(2)	0.4284(2)	0.6916(2)	0.2319(2)	3.18(6)
C(3)	0.5030(2)	0.6347(2)	0.1623(2)	3.74(7)
C(4)	0.5341(2)	0.6653(2)	0.0858(2)	4.46(8)
C(5)	0.4919(3)	0.7542(3)	0.0795(2)	4.90(8)
C(6)	0.4171(3)	0.8112(2)	0.1482(2)	4.82(8)
C(7)	0.3863(2)	0.7808(2)	0.2241(2)	4.06(7)
C(8)	0.4267(2)	0.7517(2)	0.4330(2)	3.42(7)
C(9)	0.5068(2)	0.8290(2)	0.4510(2)	4.14(7)
C(10)	0.5393(3)	0.9070(3)	0.5564(3)	5.32(9)
C(11)	0.4927(3)	0.9082(3)	0.6430(3)	5.8(1)
C(12)	0.4134(3)	0.8318(3)	0.6255(3)	5.6(1)
C(13)	0.3807(3)	0.7545(2)	0.5219(2)	4.41(8)
C(14)	0.4284(2)	0.5466(2)	0.2990(2)	3.14(6)
C(15)	0.5029(2)	0.5353(2)	0.3664(2)	3.63(7)
C(16)	0.5347(2)	0.4303(2)	0.3452(2)	4.39(8)
C(17)	0.4916(3)	0.3371(3)	0.2574(2)	4.62(7)
C(18)	0.4174(3)	0.3473(2)	0.1901(2)	4.61(8)
C(19)	0.3862(2)	0.4512(2)	0.2099(2)	3.90(7)
C(20)	-0.1251(2)	0.6715(2)	0.3521(2)	3.24(6)
C(21)	-0.1627(2)	0.6481(2)	0.4420(2)	3.10(6)
C(22)	-0.1223(2)	0.5625(2)	0.4581(2)	3.94(7)
C(23)	-0.1602(3)	0.5373(2)	0.5355(2)	4.55(8)
C(24)	-0.2384(3)	0.5957(2)	0.5970(2)	4.42(8)
C(25)	-0.2795(2)	0.6793(2)	0.5804(2)	4.11(8)
C(26)	-0.2411(2)	0.7057(2)	0.5035(2)	3.51(7)
C(27)	-0.1567(2)	0.5758(2)	0.2403(2)	3.14(6)
C(28)	-0.1018(3)	0.5545(2)	0.1509(2)	4.35(8)
C(29)	-0.1367(3)	0.4730(3)	0.0496(3)	5.30(9)
C(30)	-0.2267(3)	0.4111(2)	0.0346(2)	4.97(9)
C(31)	-0.2825(3)	0.4316(2)	0.1226(2)	4.51(8)
C(32)	-0.2474(2)	0.5132(2)	0.2247(2)	3.95(7)
C(33)	-0.1585(2)	0.7836(2)	0.3638(2)	3.25(6)
C(34)	-0.1151(3)	0.8834(2)	0.4467(2)	4.38(8)
C(35)	-0.1501(3)	0.9841(2)	0.4613(3)	5.19(9)
C(36)	-0.2295(3)	0.9881(2)	0.3953(3)	5.06(9)
C(37)	-0.2743(3)	0.8899(2)	0.3141(2)	4.61(8)
C(38)	-0.2387(2)	0.7885(2)	0.2980(2)	3.78(7)
C(39)	0.2219(2)	0.0063(2)	0.0013(2)	3.53(7)
C(40)	0.1883(2)	-0.0769(2)	-0.1150(2)	3.56(7)
C(41)	0.1103(2)	-0.0557(2)	-0.1718(2)	3.96(7)
C(42)	0.0752(3)	-0.1358(3)	-0.2757(2)	4.76(8)
C(43)	0.1181(3)	-0.2377(3)	-0.3228(3)	5.18(9)
C(44)	0.1958(3)	-0.2596(3)	-0.2665(3)	5.6(1)
C(45)	0.2311(3)	-0.1808(3)	-0.1637(3)	4.65(8)

Atom	x	y	z	B(Å)^2
C(46)	0.1888(2)	0.1244(2)	0.0315(2)	3.58(7)
C(47)	0.1238(2)	0.1788(2)	0.1138(2)	3.86(7)
C(48)	0.0935(2)	0.2855(2)	0.1378(3)	4.54(8)
C(49)	0.1267(3)	0.3368(2)	0.0794(3)	4.86(9)
C(50)	0.1907(3)	0.2828(2)	-0.0034(3)	4.97(8)
C(51)	0.2217(2)	0.1776(2)	-0.0269(2)	4.49(8)
C(52)	0.1908(2)	-0.0329(2)	0.0822(2)	3.38(6)
C(53)	0.1203(2)	-0.1217(2)	0.0522(2)	3.65(7)
C(54)	0.0878(2)	-0.1535(2)	0.1282(2)	4.34(8)
C(55)	0.1254(3)	-0.0972(2)	0.2338(2)	4.68(8)
C(56)	0.1958(3)	-0.0087(3)	0.2644(2)	4.95(9)
C(57)	0.2289(2)	0.0233(2)	0.1897(2)	4.38(8)

TABLE VI

Anisotropic Thermal Parameters for TPMCl (II)

Atom	U11	U22	U33	U12	U13	U23
Cl(1)	0.0282(3)	0.0801(4)	0.0773(4)	0.0037(3)	0.0049(3)	0.0367(3)
Cl(2)	0.0289(3)	0.0918(4)	0.0781(4)	0.0028(3)	0.0028(3)	0.0495(3)
Cl(3)	0.0341(4)	0.0704(4)	0.0910(5)	0.0035(3)	0.0015(3)	0.0411(3)
C(1)	0.024(1)	0.050(1)	0.050(1)	0.003(1)	0.002(1)	0.0222(9)
C(2)	0.032(1)	0.044(1)	0.044(1)	-0.002(1)	-0.006(1)	0.0208(9)
C(3)	0.038(1)	0.049(1)	0.055(1)	-0.001(1)	0.001(1)	0.025(1)
C(4)	0.053(2)	0.065(2)	0.051(1)	-0.008(1)	0.005(1)	0.026(1)
C(5)	0.075(2)	0.064(1)	0.051(1)	-0.017(2)	-0.009(2)	0.032(1)
C(6)	0.075(2)	0.057(1)	0.055(1)	-0.002(2)	-0.013(2)	0.031(1)
C(7)	0.051(2)	0.052(1)	0.049(1)	0.002(1)	-0.008(1)	0.022(1)
C(8)	0.040(1)	0.041(1)	0.048(1)	0.009(1)	0.001(1)	0.0197(9)
C(9)	0.049(2)	0.050(1)	0.058(1)	0.000(1)	-0.012(1)	0.026(1)
C(10)	0.072(2)	0.050(2)	0.072(2)	0.002(2)	-0.024(2)	0.024(1)
C(11)	0.095(2)	0.056(2)	0.055(2)	0.021(2)	-0.016(2)	0.016(1)
C(12)	0.090(2)	0.068(2)	0.051(2)	0.027(2)	0.007(2)	0.023(1)
C(13)	0.063(2)	0.054(1)	0.052(1)	0.015(1)	0.010(1)	0.025(1)
C(14)	0.031(1)	0.044(1)	0.047(1)	-0.002(1)	0.007(1)	0.0231(8)
C(15)	0.038(1)	0.051(1)	0.050(1)	0.004(1)	0.005(1)	0.0246(9)
C(16)	0.050(2)	0.061(1)	0.065(1)	0.013(1)	0.010(1)	0.037(1)
C(17)	0.060(2)	0.050(1)	0.060(1)	0.002(1)	0.014(1)	0.023(1)
C(18)	0.069(2)	0.045(1)	0.053(1)	-0.010(1)	0.017(1)	0.016(1)
C(19)	0.048(2)	0.051(1)	0.050(1)	-0.008(1)	0.005(1)	0.024(1)
C(20)	0.024(1)	0.056(1)	0.046(1)	0.003(1)	0.002(1)	0.0273(9)
C(21)	0.034(1)	0.045(1)	0.038(1)	0.001(1)	-0.002(1)	0.0200(8)
C(22)	0.049(2)	0.056(1)	0.049(1)	0.009(1)	0.002(1)	0.0273(9)
C(23)	0.071(2)	0.057(1)	0.051(1)	0.004(1)	-0.003(1)	0.032(1)
C(24)	0.071(2)	0.055(1)	0.039(1)	-0.011(1)	0.005(1)	0.020(1)
C(25)	0.053(2)	0.050(1)	0.048(1)	-0.004(1)	0.012(1)	0.018(1)
C(26)	0.039(1)	0.045(1)	0.050(1)	0.002(1)	0.006(1)	0.0227(9)
C(27)	0.038(1)	0.042(1)	0.044(1)	0.012(1)	0.008(1)	0.0235(8)
C(28)	0.060(2)	0.053(1)	0.055(1)	0.010(1)	0.020(1)	0.024(1)
C(29)	0.093(2)	0.055(2)	0.050(1)	0.011(2)	0.025(2)	0.020(1)

Atom	U11	U22	U33	U12	U13	U23
C(30)	0.090(2)	0.045(1)	0.048(2)	0.011(2)	-0.001(2)	0.016(1)
C(31)	0.058(2)	0.057(2)	0.053(1)	-0.001(1)	-0.009(1)	0.023(1)
C(32)	0.041(2)	0.063(1)	0.047(1)	0.001(1)	-0.001(1)	0.026(1)
C(33)	0.034(1)	0.049(1)	0.044(1)	0.000(1)	0.005(1)	0.0244(9)
C(34)	0.056(2)	0.058(1)	0.053(1)	-0.011(1)	-0.006(1)	0.027(1)
C(35)	0.084(2)	0.049(1)	0.066(2)	-0.012(2)	0.004(2)	0.029(1)
C(36)	0.082(2)	0.054(1)	0.066(2)	0.008(2)	0.009(2)	0.036(1)
C(37)	0.063(2)	0.059(1)	0.060(1)	0.013(1)	0.004(1)	0.033(1)
C(38)	0.046(2)	0.051(1)	0.046(1)	0.009(1)	0.004(1)	0.022(1)
C(39)	0.029(1)	0.049(1)	0.056(1)	0.002(1)	-0.002(1)	0.025(1)
C(40)	0.039(1)	0.049(1)	0.050(1)	0.004(1)	0.007(1)	0.0249(9)
C(41)	0.044(2)	0.053(1)	0.052(1)	0.004(1)	0.003(1)	0.023(1)
C(42)	0.059(2)	0.069(2)	0.053(1)	0.000(2)	-0.002(1)	0.029(1)
C(43)	0.076(2)	0.063(2)	0.050(2)	0.004(2)	0.008(2)	0.019(1)
C(44)	0.078(2)	0.061(2)	0.061(2)	0.019(2)	0.015(2)	0.017(1)
C(45)	0.059(2)	0.057(2)	0.057(2)	0.014(1)	0.009(1)	0.023(1)
C(46)	0.036(1)	0.045(1)	0.050(1)	-0.004(1)	-0.007(1)	0.020(1)
C(47)	0.040(1)	0.048(1)	0.057(1)	0.001(1)	-0.005(1)	0.023(1)
C(48)	0.050(2)	0.049(1)	0.063(2)	0.003(1)	-0.007(1)	0.018(1)
C(49)	0.052(2)	0.045(1)	0.083(2)	-0.004(1)	-0.014(2)	0.028(1)
C(50)	0.059(2)	0.058(1)	0.081(2)	-0.006(1)	-0.012(2)	0.042(1)
C(51)	0.049(2)	0.059(1)	0.067(2)	-0.001(1)	-0.002(1)	0.033(1)
C(52)	0.035(1)	0.045(1)	0.048(1)	0.010(1)	-0.002(1)	0.0216(9)
C(53)	0.042(2)	0.046(1)	0.051(1)	0.006(1)	-0.001(1)	0.0232(9)
C(54)	0.052(2)	0.059(1)	0.060(1)	0.004(1)	0.002(1)	0.034(1)
C(55)	0.063(2)	0.065(2)	0.056(1)	0.012(1)	0.003(1)	0.033(1)
C(56)	0.067(2)	0.070(2)	0.048(1)	0.012(2)	-0.007(1)	0.024(1)
C(57)	0.052(2)	0.053(1)	0.055(2)	0.003(1)	-0.010(1)	0.021(1)

TABLE VII

Atomic Positional and Isotropic Thermal Parameters for TPMCl (III)

Atom	x	y	z	B(Å)^2
Cl(1)	0.0543(2)	0.0173(1)	0.8915(2)	5.4(1)
Cl(2)	0.6061(2)	0.2075(1)	0.2696(2)	5.6(2)
Cl(3)	0.2209(2)	0.3934(1)	0.7126(2)	5.3(2)
Cl(4)	0.6309(2)	0.2273(1)	0.5348(2)	5.7(2)
Cl(5)	0.1629(2)	0.3840(1)	0.9498(2)	5.4(1)
C(1)	0.0333(8)	0.0093(5)	0.7491(7)	3.2(2)
C(2)	0.0957(7)	0.0749(5)	0.7228(7)	3.4(2)
C(3)	0.1528(8)	0.0753(5)	0.6400(8)	4.5(3)
C(4)	0.2038(9)	0.1361(6)	0.6121(8)	5.6(3)
C(5)	0.1983(9)	0.1951(6)	0.6671(8)	5.4(3)
C(6)	0.1419(8)	0.1954(5)	0.7481(8)	4.6(3)
C(7)	0.0912(8)	0.1354(5)	0.7767(7)	4.1(3)
C(8)	0.0684(8)	-0.0502(5)	0.6990(7)	3.4(2)
C(9)	0.0153(8)	-0.0958(5)	0.6151(7)	4.3(3)
C(10)	0.050(1)	-0.1486(5)	0.5671(8)	5.2(3)
C(11)	0.139(1)	-0.1520(5)	0.6049(8)	5.1(3)

Atom	x	y	z	B(Å)^2
C(12)	0.1952(8)	-0.1071(6)	0.6877(8)	5.1(3)
C(13)	0.160(1)	-0.0553(5)	0.7349(8)	4.9(3)
C(14)	-0.0766(8)	-0.0024(5)	0.7201(7)	3.4(2)
C(15)	-0.146(1)	-0.0466(5)	0.7669(8)	5.2(3)
C(16)	-0.247(1)	-0.0586(6)	0.7348(8)	5.7(3)
C(17)	-0.278(1)	-0.0285(6)	0.6649(9)	6.5(3)
C(18)	-0.212(1)	0.0145(6)	0.6172(9)	6.4(3)
C(19)	-0.108(1)	0.0283(5)	0.6456(8)	4.7(3)
C(20)	0.5980(8)	0.2064(5)	0.1278(7)	3.9(3)
C(21)	0.6459(8)	0.1528(5)	0.0792(7)	3.9(2)
C(22)	0.7242(9)	0.1661(5)	0.0224(8)	4.7(3)
C(23)	0.7635(9)	0.1141(6)	-0.0225(8)	5.6(3)
C(24)	0.722(1)	0.0513(6)	-0.0078(8)	5.6(3)
C(25)	0.645(1)	0.0376(6)	0.0472(9)	6.1(3)
C(26)	0.6040(9)	0.0874(6)	0.0929(8)	5.4(3)
C(27)	0.6530(8)	0.2757(5)	0.1131(7)	3.8(2)
C(28)	0.7493(9)	0.3057(5)	0.1611(7)	4.8(3)
C(29)	0.8017(8)	0.3691(6)	0.1465(8)	5.3(3)
C(30)	0.761(1)	0.4034(5)	0.0857(8)	5.2(3)
C(31)	0.667(1)	0.3752(5)	0.0385(8)	4.9(3)
C(32)	0.6140(8)	0.3112(5)	0.0530(7)	4.1(3)
C(33)	0.4900(8)	0.1885(5)	0.0852(7)	3.5(2)
C(34)	0.420(1)	0.2110(5)	0.1441(8)	5.2(3)
C(35)	0.324(1)	0.1980(6)	0.1034(9)	6.2(3)
C(36)	0.2919(9)	0.1597(5)	0.0056(9)	5.3(3)
C(37)	0.356(1)	0.1374(5)	-0.0541(8)	4.6(3)
C(38)	0.4558(9)	0.1515(5)	-0.0149(7)	4.0(3)
C(39)	0.2104(8)	0.3959(5)	0.5717(7)	3.2(2)
C(40)	0.2493(8)	0.3399(5)	0.5163(7)	3.4(2)
C(41)	0.3411(9)	0.3353(5)	0.5507(7)	4.0(3)
C(42)	0.3760(8)	0.2841(5)	0.5012(8)	4.7(3)
C(43)	0.321(1)	0.2386(5)	0.4211(8)	4.6(3)
C(44)	0.2293(9)	0.2408(5)	0.3837(7)	4.5(3)
C(45)	0.1934(8)	0.2928(5)	0.4340(7)	4.0(3)
C(46)	0.2747(8)	0.4658(5)	0.5603(7)	3.4(2)
C(47)	0.3398(8)	0.4731(5)	0.4857(7)	4.0(3)
C(48)	0.3943(8)	0.5378(6)	0.4755(8)	5.0(3)
C(49)	0.3809(9)	0.5913(6)	0.5387(9)	5.4(3)
C(50)	0.3182(8)	0.5853(5)	0.6125(8)	5.1(3)
C(51)	0.2628(8)	0.5220(5)	0.6247(7)	4.6(3)
C(52)	0.1022(8)	0.3864(5)	0.5376(7)	3.1(2)
C(53)	0.0719(9)	0.4230(5)	0.4720(7)	3.9(2)
C(54)	-0.030(1)	0.4098(5)	0.4360(8)	5.0(3)
C(55)	-0.0986(9)	0.3605(6)	0.4690(8)	5.7(3)
C(56)	-0.071(1)	0.3245(5)	0.5347(8)	5.1(3)
C(57)	0.028(1)	0.3359(5)	0.5703(7)	4.4(3)
C(58)	0.6190(8)	0.2162(5)	0.6714(7)	3.8(2)
C(59)	0.5623(8)	0.2637(5)	0.7192(7)	3.8(2)
C(60)	0.4809(9)	0.2428(5)	0.7713(8)	4.7(3)
C(61)	0.4330(8)	0.2884(6)	0.8192(7)	4.8(3)
C(62)	0.466(1)	0.3538(6)	0.8143(8)	5.5(3)

Atom	x	y	z	B(Å)^2
C(63)	0.547(1)	0.3764(5)	0.7626(8)	5.3(3)
C(64)	0.5950(8)	0.3319(6)	0.7161(8)	4.9(3)
C(65)	0.5645(8)	0.1439(5)	0.6720(8)	4.5(3)
C(66)	0.5870(8)	0.1115(5)	0.7468(7)	4.2(3)
C(67)	0.535(1)	0.0463(6)	0.7529(8)	5.5(3)
C(68)	0.458(1)	0.0145(6)	0.681(1)	7.0(3)
C(69)	0.430(1)	0.0439(8)	0.603(1)	9.5(4)
C(70)	0.484(1)	0.1102(7)	0.599(1)	7.8(4)
C(71)	0.7252(8)	0.2339(5)	0.7246(7)	3.6(2)
C(72)	0.788(1)	0.1976(5)	0.6813(8)	5.1(3)
C(73)	0.882(1)	0.2089(6)	0.7286(9)	5.8(3)
C(74)	0.916(1)	0.2557(6)	0.8189(9)	5.9(3)
C(75)	0.856(1)	0.2911(5)	0.8625(8)	5.3(3)
C(76)	0.7596(9)	0.2797(5)	0.8157(8)	4.7(3)
C(77)	0.1786(8)	0.3891(4)	1.0924(7)	3.1(2)
C(78)	0.1103(7)	0.3236(5)	1.1126(7)	3.4(2)
C(79)	0.1132(8)	0.2629(5)	1.0567(7)	4.2(3)
C(80)	0.0560(8)	0.2021(5)	1.0785(8)	4.4(3)
C(81)	-0.0042(8)	0.2030(5)	1.1571(8)	4.8(3)
C(82)	-0.0081(8)	0.2615(5)	1.2148(7)	4.3(3)
C(83)	0.0491(8)	0.3220(5)	1.1932(7)	4.0(3)
C(84)	0.1441(8)	0.4488(5)	1.1445(7)	3.1(2)
C(85)	0.1941(8)	0.4886(5)	1.2349(7)	3.9(2)
C(86)	0.1593(9)	0.5408(5)	1.2861(8)	4.8(3)
C(87)	0.076(1)	0.5513(5)	1.2432(8)	5.5(3)
C(88)	0.0265(9)	0.5120(6)	1.1531(9)	5.8(3)
C(89)	0.0592(9)	0.4602(5)	1.1016(8)	5.2(3)
C(90)	0.2859(8)	0.3973(5)	1.1248(7)	3.3(2)
C(91)	0.360(1)	0.4401(5)	1.0810(8)	5.1(3)
C(92)	0.458(1)	0.4512(6)	1.1214(9)	5.9(3)
C(93)	0.4829(9)	0.4232(6)	1.2004(8)	5.4(3)
C(94)	0.413(1)	0.3813(5)	1.2424(8)	5.1(3)
C(95)	0.3131(9)	0.3688(5)	1.2035(7)	4.1(3)

TABLE VIII

Anisotropic Thermal Parameters for TPMCl (III)

Atom	U11	U22	U33	U12	U13	U23
Cl1	0.084(3)	0.059(2)	0.055(2)	0.009(2)	0.006(2)	0.012(2)
Cl2	0.086(3)	0.080(2)	0.053(2)	0.032(2)	0.005(2)	0.012(2)
Cl3	0.079(3)	0.074(2)	0.052(2)	0.023(2)	0.012(2)	0.017(2)
Cl4	0.074(3)	0.095(3)	0.056(2)	0.032(2)	0.010(2)	0.021(2)
Cl5	0.085(3)	0.066(2)	0.049(2)	0.014(2)	0.007(2)	0.012(2)

TABLE IX

Comparison of Selected Molecular and Intermolecular Parameters for Triphenylchloromethane Polymorphs

Parameter		Phase I From Ref.1	Phase II	Phase III
C_{methyl}-Cl (Å)	Molecule 1	1.874(6)	1.851(3)	1.841(9)
	Molecule 2	1.847(6)	1.840(3)	1.847(9)
	Molecule 3	1.843(6)	1.866(3)	1.852(9)
	Molecule 4			1.850(9)
	Molecule 5			1.847(9)
Cl·····Cl (Å)[a]	Molecules 1-1'[b]	3.583(2)	3.547(2)	3.383(8)
	Molecules 2-3	3.209(2)	3.225(2)	3.268(8)
	Molecules 4-5			3.407(8)
C_{methyl}·····C_{methyl} (Å)				
	Molecules 1-1'	5.870(7)	5.759(4)	6.46(1)
	Molecules 2-3	6.301(7)	6.242(4)	6.23(1)
	Molecules 4-5			6.02(1)
C_{phenyl}-C_{methyl}-Cl (deg)				
	Molecule 1	106.2(3)	105.9(2)	106.6(6)
			106.5(2)	106.7(6)
			106.1(2)	108.4(6)
	Molecule 2	106.0(3)	106.4(2)	105.9(6)
			107.9(2)	107.0(7)
			106.5(2)	109.4(7)
	Molecule 3	107.0(3)	106.7(2)	106.3(6)
			105.5(2)	106.5(6)
			106.2(2)	107.6(6)
	Molecule 4			106.3(7)
				109.2(7)
				106.4(7)
	Molecule 5			105.7(6)
				107.3(6)
				108.6(6)
C_{methyl}-Cl·····Cl (Å)[c]				
	Molecules 1-1'	180	176.1(1)	170.8(4)
	Molecules 2-2'	180	175.0(1)	174.7(4)
	Molecules 3-3'	180	173.5(1)	173.3(4)
	Molecules 4-4'			176.5(4)
	Molecules 5-5'			172.4(4)

[a]Nearest intermolecular Cl-Cl contacts.

[b]Prime denotes distance or angle between atoms in symmetry related molecules.

[c]Deviations from the linear ($P\bar{3}$) arrangement as measured by largest angle between C_{methyl}-Cl axis and Cl·····Cl vector between translationally related chlorines.

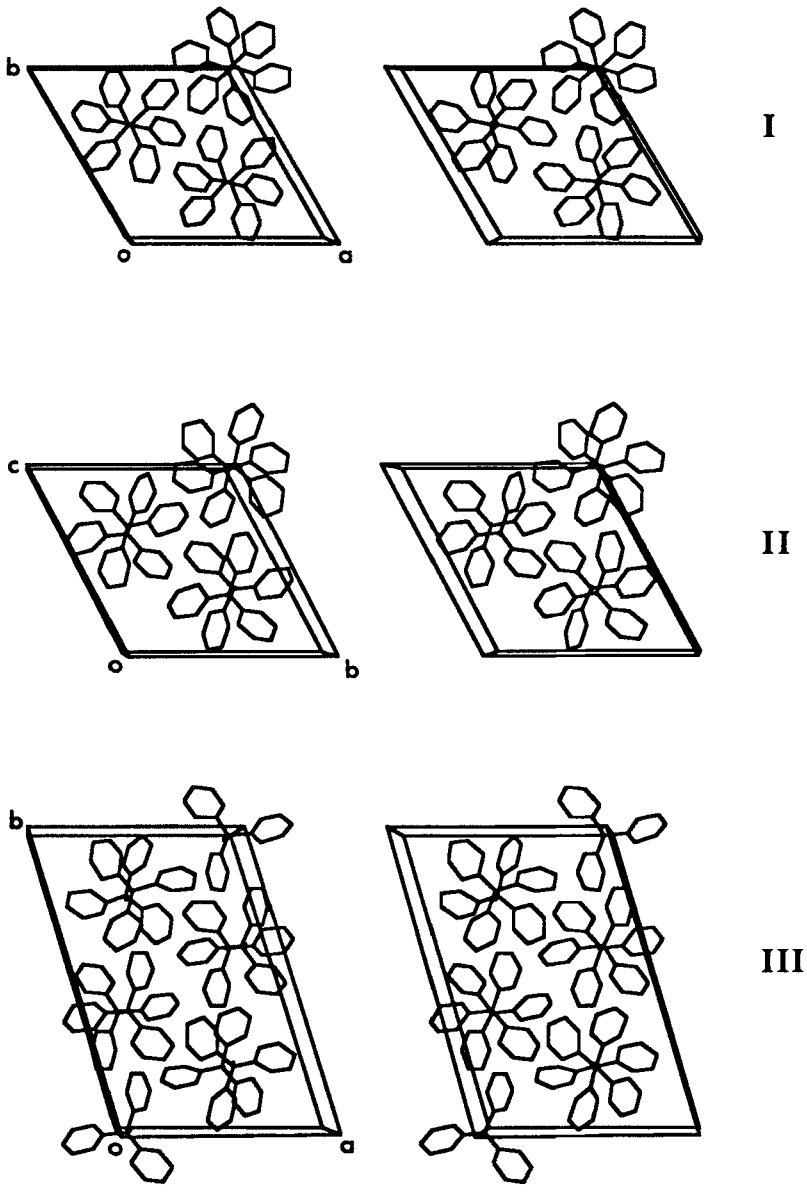

FIGURE 2. Stereoviews of the packing of **I**, **II**, and **III** along *c*, *a*, and *c*, respectively. Hydrogen atoms have been deleted for clarity. Picture of **I** based on coordinates from ref. 1.

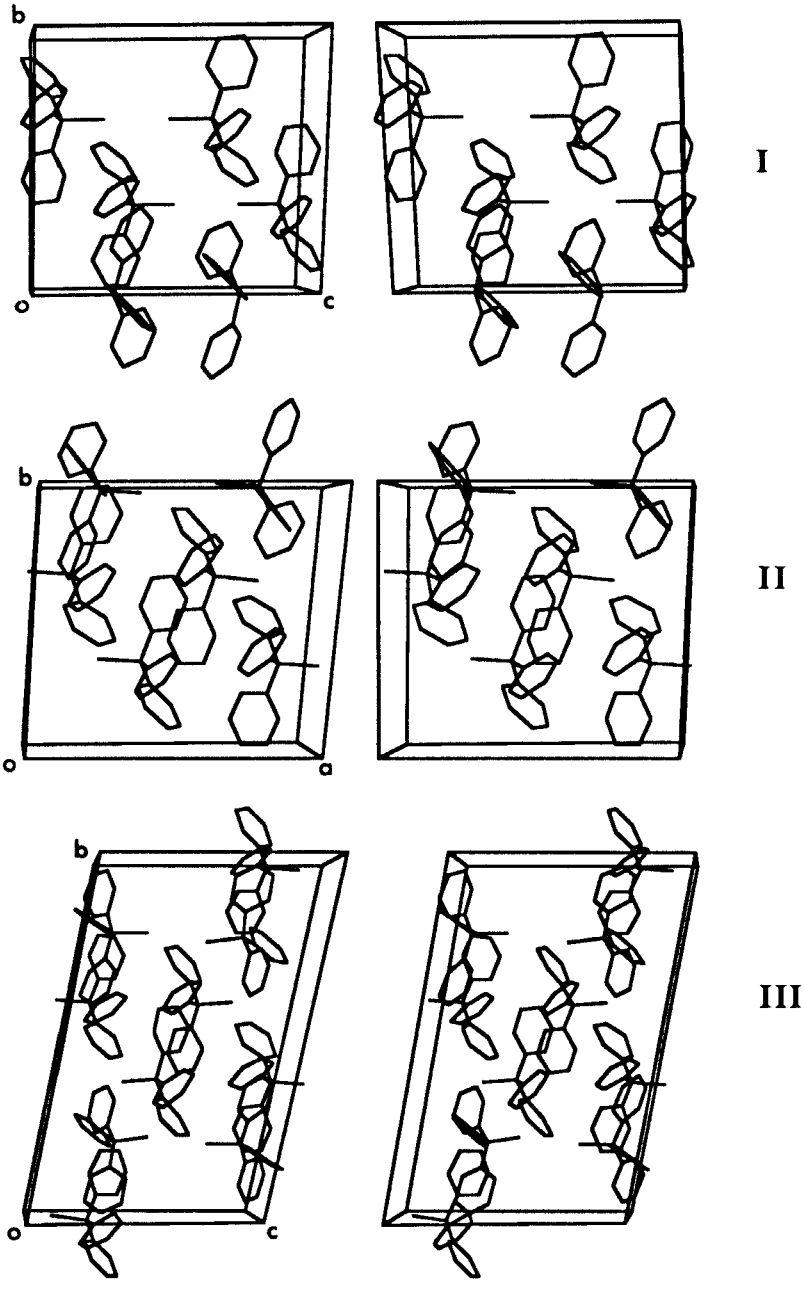

FIGURE 3. Stereoviews of the packing of **I**, **II**, and **III** along *a*, *c*, and *a*, respectively. Hydrogen atoms have been deleted for clarity. Picture of **I** based on coordinates from ref. 1.

3. DIFFERENTIAL SCANNING CALORIMETRY

Thermograms of crystals of TPMCl grown by slow evaporation of pentane or ether solutions containing a small amount of acetyl chloride show three transitions corresponding to transformations of the three phases at 99°C (**III**), 108°C (**II**), and 111°C (**I**), respectively. As earlier reported by Gerdil and Dunand[6], phase **I** may be isolated from carbon tetrachloride or benzene. Thermograms of the isolated samples showed fusion between 112°-115°C, varying from sample to sample. Phase **III** may be isolated from 7/3 petroleum ether/benzene. Fusion was indicated between 98°-101°C. Phase **II** may be enriched by rapid evaporation but we were unable to isolate samples of **II** uncontaminated by the presence of a small quantities of **III** as evidenced by a small peak in the thermogram at 99°C. Visual confirmation of melting was obtained using a hot stage melting point apparatus (mp 99-101°). Isolated samples of **III** show a single transition indicating fusion. The enthalpy of fusion was calculated as 16.5±0.2cal·g^{-1}. The enthalpy of fusion for **I** was calculated as 17.1±0.5cal·g^{-1}.[12] Although it seems likely that **II** transforms to **I** prior to melting, our inability to isolate this phase precludes a confirmation of this supposition.

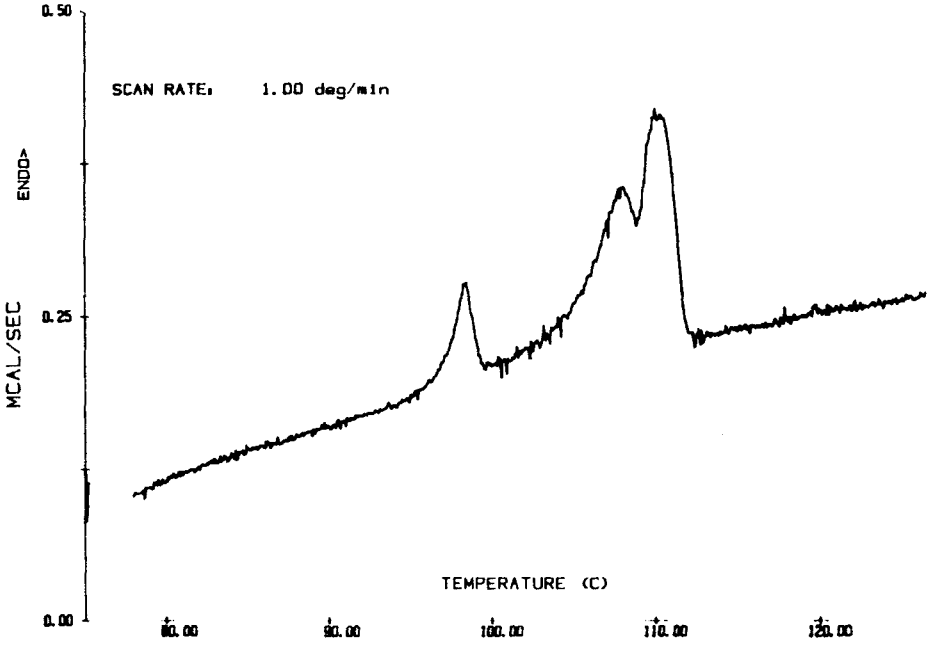

FIGURE 4. Thermogram of the polymorphous precipitate of TPMCl grown from pentane containing ~0.5% acetyl chloride.

4. EXPERIMENTAL

Triphenylchloromethane (TPMCl) and triphenylacetic acid (TPMCOOH) were obtained from the Aldrich Chemical Company and recrystallized without further purification. All TPMCl crystallization solvents were dried over molecular sieves (4A) and several drops of acetyl chloride were added to each crystallization vial to prevent hydrolysis of the chloride. Crystallizations were carried out by evaporation in glass vials with punctured polyethylene caps.

4.1 X-ray Crystallography

Single crystals of TPMCOOH, $C_{20}H_{16}O_2$, grown by slow evaporation from chloroform at room temperature, had the form of hexagonal prisms with well-defined {0001} faces. Graphite monochromated intensities (CuKα, λ=1.54178Å) of a crystal (0.51x0.39x0.26mm) mounted on a glass fiber with epoxy were measured on a Nicolet R3m diffractometer equipped with a nitrogen flow cooling apparatus. Cell constants were determined by a least-squares fit of 23 diffractometer-measured reflections ($40°<2\theta<50°$) at 175K. The material belongs to the trigonal system, space group $P\bar{3}$, with $a=b$=14.105(3)Å, c=13.121(2)Å, V=2261(1)Å^3. A density of 1.27g·cm^{-3} was calculated for Z=6, M=288.3 g·mol^{-1}, μ=6.5cm^{-1}.

Intensities were measured with an ω-scan at a variable rate. Background counts were recorded for half the scan time at each extreme of the 1.0° scan range. Crystal decomposition was monitored by remeasuring standard reflections. Intensities were reduced by applying Lorentz, polarization, and absorption corrections (psi-scans). Equivalent reflections were averaged to give 2864 unique data of which 2569 with $F_o>3\sigma(F_o)$ were considered observed.

The structure was solved by direct methods employed in the SHELXS86 program and refined using a blocked-diagonal least-squares procedure. All non-hydrogen atoms were refined with anisotropic thermal parameters. Oxygen atoms were constrained with a site occupancy of 0.33333 as were the carbon atoms on special positions. The phenyl hydrogens were included at ideal positions (C-H = 0.96Å, C-C-H = 120°) and varied using a riding model. The acidic hydrogens were fixed at the midpoint between neighboring oxygens in the the dimers. Refinement converged at R=0.062, R_w=0.074 for 135 parameters. The final difference map was featureless with a maximum peak of 0.3e·Å^{-3}.

The triclinic modification of TPMCl, **II**, was grown by slow evaporation of a pentane solution to which a drop of acetyl chloride had been added. Crystals of **I**

may also be obtained under these conditions. Graphite monochromated intensities (MoKα, λ=0.71073Å) of a crystal (0.31x0.19x0.17mm) mounted on a glass fiber with epoxy were measured on a Enraf-Nonius CAD4 diffractometer equipped with a nitrogen-flow cooling apparatus. Cell constants were determined by a least-squares fit of 25 diffractometer-measured reflections ($19°<2\theta<25°$) at 228K. The material belongs to the triclinic system, space group $P\bar{1}$, with a=13.028(1)Å, b=13.559(2)Å, c=13.969(3)Å, V=2179(1)Å^3. A density of 1.27g·cm^{-3} was calculated for Z=6, M=278.8 g·mol^{-1}, μ=2.47 cm^{-1}.

Intensities were measured with an ω-2θ scan at a variable rate. Background counts were recorded for half the scan time at each extreme of the scan range. Crystal decomposition was monitored by remeasuring standard reflections. Intensities were reduced by applying Lorentz, polarization, and absorption corrections (Psi-scans). Of the 7667 unique reflections 4828 with $F_o>3\sigma(F_o)$ were considered observed.

The structure was solved by direct methods employed in the SHELXS86 program and refined using a full-matrix least-squares procedure. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl hydrogens were included at ideal positions (C-H = 0.96Å, C-C-H = 120°) and varied using a riding model. Refinement converged at R=0.045, R_w=0.058 for 536 parameters. The final difference map was featureless with a maximum peak of 0.2e·Å^{-3}.

The triclinic modification of TPMCl, **III**, was grown as were **II** although at a slower rate of evaporation. Forms **II** and **III** often co-precipitate during the same crystallization. Graphite monochromated intensities (CuKα, λ=1.54178Å) of a crystal (0.35x0.35x0.08mm) mounted on a glass fiber with epoxy were measured on a Rigaku AFC5 diffractometer equipped with a nitrogen flow cooling apparatus. Cell constants were determined by a least-squares fit of 25 diffractometer-measured reflections ($45°<2\theta<55°$) at 248K. The material belongs to the triclinic system, space group $P\bar{1}$, with a=14.1562(4)Å, b=21.3190(7)Å, c=13.0654(5)Å, α=99.92(3)°, β=92.68(3)°, γ=106.15(2)°, V=3712(2)Å^3. A density of 1.25g·cm^{-3} was calculated for Z=10, M=278.8 g·mol^{-1}, μ=17.32cm^{-1}.

Intensities were measured with an ω-2θ scan at a variable rate. Background counts were recorded for half the scan time at each extreme of the scan range. Crystal decomposition was monitored by remeasuring standard reflections. Intensities were reduced by applying Lorentz, polarization, and absorption corrections (Psi-scans). Of the 3751 unique reflections 2737 with $F_o>3\sigma(F_o)$ were considered observed. High angle data were not collected ($2\theta>80°$).

The structure was solved by direct methods employed in the MITHRIL program and refined using a full-matrix least-squares procedure. Only chlorine atoms were refined anisotropically due to a paucity of data. The phenyl hydrogens were included at ideal positions (C-H = 0.96Å, C-C-H = 120°) and varied using a riding model. Refinement converged at R=0.064, R_w=0.084 for 135 parameters. The final difference map was featureless with a maximum peak of 0.4e·Å^{-3}.

4.2 Differential Scanning Calorimetry

Phase transformations were recorded using a Perkin-Elmer DSC-4 Differential Scanning Calorimeter with a Thermal Analysis Data Station. The DSC was calibrated with an indium standard (mp=157.4°C, onset 156.6°C, ΔH_f=6.8 cal·g^{-1}). The samples were prepared by quickly grinding the solid into a fine powder with an agate mortar and pestle and then sealing ~3mg within aluminum pans. Peak profiles were insensitive to scan rates varying from 1-10°·min^{-1}. Thermograms were typically recorded at a scanning rate of 5°C·min^{-1}.

CONCLUSION

McCrone pointed out that polymorphism is more common in substances whose physical properties have been intensively studied.[13] Dunitz and coworkers cautioned that this observation belies the fact that polymorphs are often overlooked in cursory X-ray studies in which molecular structure is the principle aim.[3] Therefore, perhaps it is not surprising that structures of the metastable triclinic modifications of TPMCl were determined only in the context of a closer examination of the stable structure.

Polymorphism in molecular crystals is often described as conformational; in such cases there are persistent differences in molecular geometries due to the accessibility of several low lying conformers. The polymorphism in such cases is undoubtedly due, in part, to the structural variability of the constituent molecules. It is rare indeed to find eleven crystallographically independent molecules by diffraction as in TPMCl. It is particularly unusual in a molecule with one well-defined conformation.[14] We have shown trivial metric differences among the eleven structures. Here, the polymorphism is inherently "intermolecular" in origin. However, it is not readily apparent which forces preclude the collapse of the triclinic structures. Preliminary data points to a fourth polymorph of TPMCl, whose structure remains unsolved at this time. Future work will focus on this structure and fuller analysis of the differences between **I**, **II**, and **III**.

ACKNOWLEDGMENT

We thank the Petroleum Research Foundation (24331-G6) for support of this work. In addition, BK thanks Kurt Mislow and J.M. McBride for support of preliminary work and JMM for the use of his calorimeter. Supplementary Material Available: Observed and calculated structure factors, and hydrogen atom positions with isotropic thermal parameters (79 pages) have been deposited with the British Library Document Center as Supplementary Publication No. 90264. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

REFERENCES

1. B. Kahr, J.M. Chance, K. Mislow, unpublished; J.M. Chance, Dissertation, Princeton University, 1988.

2. A. Dunand and R. Gerdil, *Acta. Cryst., Sect. B*, **B38**, 570 (1982).

3. See for example: M. Egli, J.D. Wallis, J.D. Dunitz, *Helv. Chim. Acta*, **69**, 255 (1986).

4. A. Dunand and R. Gerdil, *Acta. Cryst., Sect. B*. **B40**, 59 (1984).

5. This is a common packing motif for triphenylmethyl-X derivatives. See the crystal structure of triphenyliodomethane: B. Kahr, Dissertation, Princeton University, 1988.

6. R. Gerdil and A. Dunand, *Acta. Cryst., Sect. B*. **B31**, 936 (1975).

7. In ref. 1 the authors remarked in a footnote that A.N. Winchell (*The Optical Properties of Organic Compounds*, New York: Academic Press, 1954) cited a triclinic form of TPMCl observed by J. Young (BS Thesis, Massachusettes Institute of Technology, 1931). The correct reference is to the 1931 Thesis of R.W. Hartline (*Optical and Crystallographic Constants of Crystalline Organic Compounds*) who refers to TPMCl as "monoclinic or trigonal" and cites a private communication from R.C. Young. Therefore, it is by no means clear from the literature that a triclinic form of TPMCl was observed prior to the work of Gerdil and Dunand (ref 3).

8. TPMCOOH had been indexed previously by McCrone and coworkers using powder X-ray diffraction data. See: O.W. Adams and W.C. McCrone, *Anal. Chem.* **27**, 1033 (1955).

9. Several triphenylacetate crystal structures have been previously reported. See: F.A. Cotton and J.Lon Thompson, *Inorg. Chim. Acta*, **81**, 193 (1981); F.A. Cotton, X. Feng, P.A. Kibala and M. Matusz, *J. Am. Chem. Soc.* **110**, 2807 (1988); R.J. Kulawiec, R.H. Crabtree, G.W. Brudvig, G.K. Schulte, *Inorg. Chem.* **27**, 1311 (1988).

10. J. Landais, *Bull. Soc. Chim. Fr.* 648 (1953). See also: C. Stora and N. Poyer, *Ibid.* 841 (1966).

11. V. Sona and N. Gautham, *Acta Cryst. Sect. B*, **B48**, 111 (1992).

12. M. Naoki, M. Seki, H. Kugo, F. Saito, and T. Tanioka, *J. Phys. Chem.* **95**, 5628 (1991).

13. W.C. McCrone, in *Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M.M. Labes, and A Weissenberger (Wiley Interscience, New York, 1965, Vol. II, Chapter 8).

14. K.M. Mislow, *Acc. Chem. Res.* **9**, 26 (1976) and references within.