Structure, Optical Resolution, and Conformational Stability of Perchlorotriphenylamine

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Abstract: The structure of perchlorotriphenylamine has been determined by X-ray analysis. Because this molecular propeller occupies a crystallographic site of C_2 symmetry, the nitrogen atom is located in the plane of the neighboring carbon atoms. Partial resolution was achieved by chromatography on microcrystalline cellulose triacetate. Perchlorotriphenylamine thus becomes the first example of an optically active compound of the type Ar_3Z or Ar_3ZX in which Z is not a chiral center. The compound is optically stable under ordinary conditions, and elevated temperatures are required for racemization. The activation energy (E_a) for this process, 28.0 kcal/mol, slightly exceeds an empirical force field estimate of 25-27 kcal/mol calculated for the racemization barrier in the sterically similar trimesitylamine.

In the course of our studies on molecular propellers,[2] empirical force field calculations were employed to estimate the energy requirements for enantiomerization of compounds in which three mesityl (2,4,6-trimethylphenyl) groups are attached to a common atomic center.[3] Enantiomerization results from a reversal of propeller helicity; the mechanism of lowest energy (threshold mechanism) for this process is the two-ring flip, in which two of the mesityl rings rotate in the same direction through a conformation in which the plane of the ring is perpendicular to the reference plane (defined as the plane containing the three carbon atoms attached to the central atom), while the third rotates in the opposite direction. A salient result was the prediction[3] of a 25-27 kcal/mol enantiomerization barrier for trimesitylamine (**1**), suggesting that **1** "should be resolvable and optically stable at room temperature". It had previously been noted[4] that the enantiomerization barrier observed (by dynamic NMR) for trimesitylmethane, 21.9 kcal/mol at 167 °C, implies a half-life for racemization of ca. 2 h at 0 °C. The substantially greater conformational stability predicted for **1** may be attributed principally to the relatively short C-N bond length (1.42 Å in triphenylamine, as compared to C_{ar}-CH bond lengths of 1.53 and 1.54 Å in triphenyl- and trimesitylmethane, respectively); this results in a more compact ground-state structure and consequently in a more strained transition state for the enantiomerization of **1**.

Attempts to subject this prediction to a direct test foundered, since efforts to prepare **1** or the sterically related tris(2,6-dimethylphenyl)amine were unsuccessful. Evidently, the same factor which is responsible for a high racemization barrier, i.e., intramolecular congestion, militates against the synthesis of this crowded structure by the usual condensation methods. Thus, although we succeeded in preparing bis(2,6-dimethylphenyl)amine,[5] a compound which had resisted previous attempts at synthesis,[6,7] efforts to incorporate a third 2,6-dimethylphenyl ring in the structure proved abortive. We therefore resorted to an alternative approach.

Since methyl and chloro groups are commonly regarded as having comparable steric requirements,[9] one might expect similarities in the static and dynamic stereochemistry of **1** and tris(2,4,6-trichlorophenyl)amine. Although the latter is unknown, the perchlorinated compound, tris(2,3,4,5,6-pentachlorophenyl)amine or perchlorotriphenylamine (**2**), has been known for over a century. In common with the first report of its synthesis by Ruoff in 1876,[12] all subsequent preparations[13-15] of **2** have involved exhaustive chlorination of triphenylamine.[16] Accordingly, we undertook a study of the stereochemistry of this compound, on the assumption that, with respect to its conformational behavior, **2** represents a satisfactory model for **1**.

Results and Discussion

Molecular Structure. The ground-state structure of **2** was determined by X-ray analysis (cf. Table I and Figure 1). The molecule occupies a crystallographic site of C_2 symmetry (the twofold axis passes through N, C11, C14, and Cl14) but the three C-N bond lengths (1.414, 1.430, and 1.430 Å), the three C-N-C bond angles (121.6, 119.2, and 119.2°), and the three ring tilt angles[18] (35, 40, and 40°) are all very similar in magnitude, and deviation from perfect propeller shape (D_3 symmetry) is therefore slight. The position of the C_2 axis constrains the nitrogen atom to lie in the reference plane. Although such strict planarity of nitrogen in a triarylamine appears to be unprecedented, the displacement of this atom from the reference plane in previously reported X-ray structures of triarylamines[19] is so slight (≤ca. 0.1 Å) that nonplanarity in these cases may be ascribed to the accident of crystal packing.[20,22] To a remarkable degree, the structure of **2** resembles that of trimesitylborane,[25] which also lies on a C_2 axis in the crystal, and which has mesityl tilt angles of 39, 40, and 40°.[26] Presumably, the structures of perchlorotriphenylmethyl radical,[28] cation,[29] and anion[30] are also very similar to that of **2**.[31]

Despite its compactness, the molecular structure of **2** is not significantly deformed. All C-C and C-Cl bond distances are normal (1.39 ± 0.01 and 1.72 ± 0.01 Å, respectively), and, with the exception of C1-N-C1′, C2-C1-C6, and C12-C11-C12′ (121.6, 117.8, and 117.9°, respectively), all bond angles fall within the narrow range of 119-121°. Furthermore, the six carbon atoms in each ring are coplanar to within ±0.005 Å. Strain-induced distortions are only found near the center of the molecule, where steric interactions are relatively severe. Besides the three angle deformations noted above, out-of-plane deformations of the chlorine atoms (−0.068, −0.013, 0.002, 0.054, 0.080, 0.098, 0.014, and 0.000 Å for Cl2-6 and Cl12-14, in that order) are most marked in the ortho positions of the benzene rings, i.e., for Cl2, Cl6, and Cl12 (by way of sign calibration, C11 is on the positive side of the C1-C6 ring plane). None of these deformations, however, can be described as major.

Optical Resolution. Derivatization of the nitrogen atom in **2** for purposes of optical resolution is prevented by an extraordinary lack of reactivity. Unlike triphenylamine, **2** does not form salts[32] and is immune to oxidation by nitric acid or chlorine.[15] As in the case of the closely related perchlorotriphenylmethyl species,[28-30] the chemical inertness of **2** is principally a consequence, first, of the steric shielding provided by the six ortho chlorines, which encapsulate the nitrogen atom

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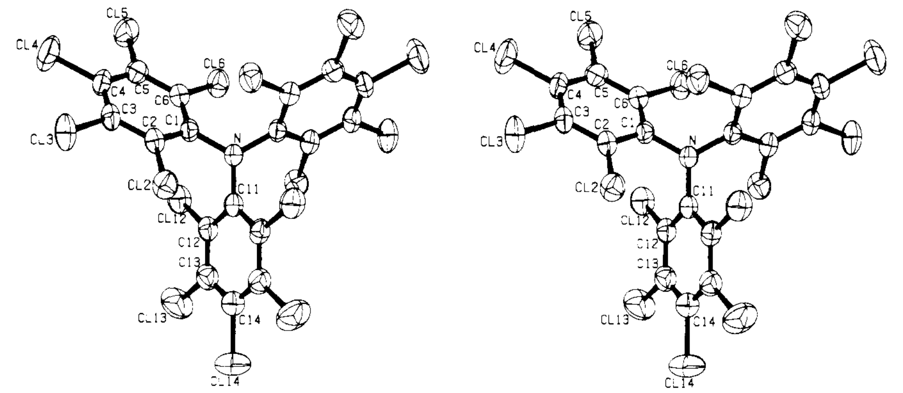

Figure 1. Stereoview of the X-ray structure of perchlorotriphenylamine (**2**).

Table I. Final Atomic Coordinates for Perchlorotriphenylamine (**2**)[a]

atom	*x*	*y*	*z*
Cl (2)	0.149 53 (8)	0.516 12 (13)	0.629 07 (10)
Cl (3)	−0.009 39 (8)	0.642 36 (16)	0.584 72 (11)
Cl (4)	−0.057 89 (9)	0.842 41 (17)	0.421 44 (14)
Cl (5)	0.054 56 (9)	0.908 22 (14)	0.297 46 (12)
Cl (6)	0.213 86 (8)	0.777 73 (14)	0.335 66 (10)
Cl (12)	0.146 10 (8)	0.473 29 (13)	0.308 71 (9)
Cl (13)	0.143 62 (11)	0.201 59 (15)	0.313 35 (14)
Cl (14)	0.250 00	0.062 95 (21)	0.500 00
N	0.2500	0.5896 (5)	0.5000
C (1)	0.1765 (3)	0.6515 (5)	0.4811 (3)
C (2)	0.1244 (3)	0.6228 (5)	0.5348 (3)
C (3)	0.0528 (3)	0.6811 (5)	0.5157 (4)
C (4)	0.0312 (3)	0.7701 (5)	0.4439 (4)
C (5)	0.0827 (3)	0.8006 (5)	0.3905 (4)
C (6)	0.1542 (3)	0.7421 (5)	0.4084 (4)
C (11)	0.2500	0.4639 (6)	0.5000
C (12)	0.2025 (3)	0.4001 (5)	0.4167 (4)
C (13)	0.2023 (3)	0.2768 (5)	0.4175 (4)
C (14)	0.2500	0.2156 (7)	0.5000

[a] Standard deviations in parentheses.

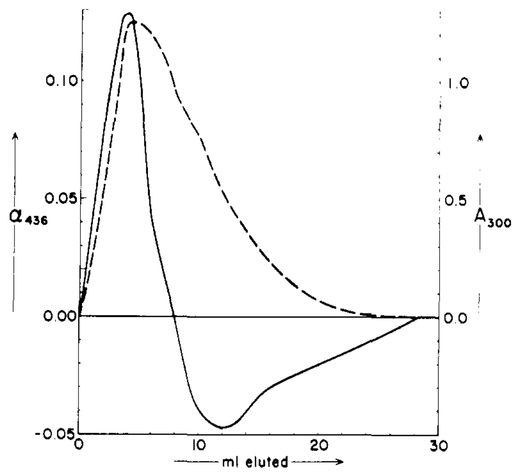

Figure 2. Chromatography of 50 mg of (±)-**2** in 1:1 CCl_4-ethanol on 40 g of microcrystalline triacetylcellulose (particle size 0.05–0.07 mm). Column dimension 38 × 2 cm. Solid line: rotation (α) of eluate at 436 nm, l 1 dm. Dashed line: absorbance (A) at 300 nm of eluate diluted by a factor of 125 with CCl_4, l 1 cm. The abscissa gives the volume of eluate following a forerun containing no **2**.

and thus render it virtually impregnable to reagent attack, and, second, of the prohibitive overcrowding which would result from the need to accommodate three pentachlorophenyl ligands in the coordination sphere of any reaction product with a tetracoordinate nitrogen atom. The lack of reactivity of trimesitylborane, which, as was noted above, is structurally similar to **2**, supports the notion that these steric factors are primarily responsible for the inertness of **2**, though the high electron-withdrawing character of the three pentachlorophenyl ligands may play a contributing role. Manual separation of enantiomeric crystals is precluded by the centrosymmetric crystal structure of **2**, which packs two racemic pairs per unit cell. Various attempts to prepare derivatives of **2** containing a ring substituent, e.g., a carboxy group, suitable as a handle for resolutions proved fruitless.[34] With alternative options closed, we therefore turned to the method of resolution by liquid chromatography on a chiral stationary phase.[35]

The recent development of microcrystalline cellulose triacetate as a versatile and stereoselective stationary support for the direct chromatographic separation of enantiomers[36] constitutes a major advance in resolution methodology.[37] In utilizing this approach we banked on the breadth of its applicability. Our expectations were not disappointed: chromatography of **2** on microcrystalline cellulose triacetate did indeed lead to the desired optical resolution. Using 1:1 CCl_4-ethanol as eluent, (+)-**2** was eluted first, followed by (−)-**2** (Figure 2). However, as indicated by the UV absorption of the eluted fractions, there was significant overlap between the enantiomeric components, and we can therefore claim no more than partial resolution. For the present, the enantiomeric excess in the optically active fractions remains unknown.

To the best of our knowledge, **2** is the first example of an optically active compound of the type Ar_3Z or Ar_3ZX in which Z is not a chiral center. A theoretical model relating structure and signed rotational strength in molecular propellers has been developed,[38] but a discussion of the absolute configuration[39] and rotational strength of **2** must await the completion of ancillary studies, including continuing efforts to determine the absolute rotation[42] of **2**.

Racemization Studies. Racemization of (+)- and (−)-**2** in hexachloro-1,3-butadiene was monitored polarimetrically as a function of time (for details see Experimental Section). The process was found to follow strict first-order kinetics (Table II). Activation parameters obtained from these data were E_a = 28.0 kcal/mol; $A = 1.1 \times 10^{11}$ s^{-1}; $\Delta H^{\ddagger} = 27.2 \pm 0.5$ kcal/mol; $\Delta S^{\ddagger} = -10.8 \pm 1.2$ gibbs/mol; $\Delta G^{\ddagger} = 31.4 \pm 0.7$ kcal/mol at 120 °C. The high racemization barrier qualifies **2** as the latest addition to the growing list of configurationally stable[43] organic molecules belonging to the chiral point group D_3.[44,45]

The values of A and $\Delta S^{\ddagger}$ are typical of processes involving restricted rotation,[46] and may indicate a loss of internal degrees of freedom in the transition state to enantiomerization, presumably by the two-ring flip mechanism. The magnitude of the activation energy (E_a) or enthalpy ($\Delta H^{\ddagger}$) for racemization slightly exceeds the calculated estimate of 25–27 kcal/mol for

Table II. Racemization Kinetics of Perchlorotriphenylamine (**2**) in Hexachloro-1,3-butadiene

temp, °C	151.8	136.9	120.9	120.9[b]
sample concn, g/25 mL	0.2569	0.3434	0.2166	0.2166
no. of data points	10	11	13	9
length of run, s	3300	7200	14 500	12 400
aliquot rotation α, deg[a] (initial/final)				
589 nm	+0.048/+0.015	+0.059/+0.023	−0.102/−0.065	−0.083/−0.057
546	+0.055/+0.014	+0.067/+0.025	−0.128/−0.083	−0.106/−0.072
436	+0.107/+0.026	+0.127/+0.050	−0.253/−0.168	−0.208/−0.141
first-order rate constant 10^5k, s^{-1} (r)[c]				
589 nm	36.5 (0.9973)	12.7 (0.9949)	2.90 (0.9909)	3.04 (0.9937)
546	41.8 (0.9985)	13.7 (0.9976)	2.95 (0.9984)	3.14 (0.9979)
436	43.0 (0.9986)	13.3 (0.9986)	2.86 (0.9992)	3.15 (0.9994)

[a] l 1 dm, 32 °C. The initial rotation refers to the first aliquot portion, withdrawn after a 5-min period of sample immersion at the stated temperature. [b] Duplicate run. [c] Correlation coefficient.

the corresponding barrier in **1**. Considering the approximations inherent in the empirical force field calculations,[3] one may regard the barrier heights calculated for **1** and found for **2** as being in satisfactory agreement. Indeed, the agreement becomes even more remarkable if two particular weaknesses in the original assumption, that **2** represents a satisfactory model for **1**, are taken into account. First, it has to be recognized that this model ignores the likely action of buttressing effects, by which the presence of chloro groups in the 3 and 5 positions would serve to increase the effective size of the chloro groups in the "blocking" 2 and 6 positions. A similar situation was recently encountered in a study of rotational barriers of 9-alkyl groups in 1,4-dimethyl- and 1,2,3,4-tetrachlorotriptycenes, where it was found[47] that the steric requirement of the 1-chloro group appeared to be significantly greater than that of the 1-methyl group; in this case also, the effect was thought to be attributable to buttressing.[48] Second, the force field model[3] ignores electronic effects, and in **2** one may suspect the operation of inductive effects due to the chlorine atoms, as well as of resonance effects due to delocalization of the nitrogen lone pair. The good agreement between calculated and found barriers therefore indicates that in the process under consideration such effects are of minor importance, or else happen to cancel fortuitously.

In view of their family resemblance to **2**, perchlorotriphenylmethyl radical and the derived ions may also be obtainable in optically active forms.

Experimental Section

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. NMR spectra were recorded on a Varian A-60 or XL-100 spectrometer and chemical shifts refer to tetramethylsilane as internal reference. Melting points are corrected. Optical rotations were measured at ambient temperatures in 1-dm tubes on a Perkin-Elmer Model 141 polarimeter, and UV spectra on a Cary 14 spectrophotometer.

Bis(2,6-dimethylphenyl)amine.[5] A mixture of 2,6-dimethylaniline (3.0 g), 2,6-dimethyliodobenzene (11.5 g), copper powder (0.5 g), potassium carbonate (6.8 g), and nitrobenzene (20 mL) was heated under reflux for 48 h. The reaction mixture was filtered through glass wool, and the volatile components were removed by distillation at 100 °C (1 Torr). The remaining black residue was dissolved in petroleum ether and chromatographed on silica gel. Elution with 30-60 °C petroleum ether yielded the desired product in the head fraction. Recrystallization from methanol afforded a white, crystalline solid (0.75 g, 13%), mp 107-108 °C. The ^1H NMR spectrum featured resonances at δ ($CDCl_3$) 1.9 (s, 12 H, CH_3), 4.6 (br s, 1 H, NH), and 6.8 (m, 6 H, aromatic H) ppm. The IR spectrum (Nujol mull) displayed a strong absorption at 3380 cm^{-1} (NH stretch).

Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.02; H, 8.37; N, 6.26.

A mixture of bis(2,6-dimethylphenyl)amine, 2,6-dimethyliodobenzene, copper powder, potassium carbonate, and nitrobenzene was heated under the conditions described above. No trace of tris(2,6-dimethylphenyl)amine could be detected (MS) even after a 72-h reflux period.

Perchlorotriphenylamine (2). Preparation. Triphenylamine was perchlorinated according to the procedure of Baker et al.[14] The product was recrystallized from carbon tetrachloride and dimethylformamide, sublimed at 290 °C (0.3 Torr), and once more recrystallized from dimethylformamide. This procedure yielded colorless crystals, mp 370-376 °C dec (lit.[14] 363 °C), which were suitable for X-ray analysis. The ^{13}C NMR spectrum (25.2 MHz, $CDCl_3$-CCl_4, 0.1 mol $Cr(acac)_3$/mol **2**) displayed four singlets at δ 131.5, 131.9, 133.5, and 139.8 ppm, with relative intensities of ca 2:1:2:1. By analogy with the ^{13}C chemical shifts for triphenylamine,[49] we assign the above resonances to the 2,6, 4, 3,5, and 1 carbons of **2**, respectively.[45] UV: λ_{max} (CCl_4) 300 nm (ϵ 29 870) and 255 (32 880).

Anal. Calcd for $C_{18}Cl_{15}N$: C, 28.37; H, 0.00; Cl, 69.79. Found: C, 28.38; H, 0.00; Cl, 70.15.

Warning. Precautions should be observed against skin contact or inhalation of this or other polyhalogenated compounds.[50]

Crystallography. Crystals of **2**, obtained from dimethylformamide, are monoclinic, space group $A2/a$, with $a = 17.767$ (4) Å, $b = 11.258$ (2) Å, $c = 13.820$ (3) Å, $\beta = 108.44$ (1)°, and $d_{calcd} = 1.929$ g cm^{-3} for $Z = 4$ ($C_{18}Cl_{15}N$, $M = 762.00$). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ-2θ scans, pulse height discrimination). A crystal measuring approximately 0.10 × 0.12 × 0.30 mm was used for data collection; the data were corrected for absorption ($\mu = 145.5$ cm^{-1}). A total of 1773 reflections were measured for $\theta < 57°$, of which 1340 were considered to be observed ($I > 2.5\sigma(I)$). The structure was solved by a multiple solution procedure[51] and was refined by full-matrix least squares. In the final refinement anisotropic thermal parameters were used for all atoms. The final discrepancy indices are $R = 0.038$ and $wR = 0.040$ for the 1340 observed reflections. The final difference map has no peaks greater than ±0.4 e A^{-3}. Final atomic coordinates are listed in Table I, and a stereoview of the final structure is given in Figure 1.

Optical Resolution. A suspension of 40 g of microcrystalline cellulose triacetate[36] (particle size 0.05-0.07 mm) in ethanol was heated for ca. 10 min. A chromatography column (i.d. 2 cm) was packed with the cooled slurry, to a height of 38 cm. The packed column was washed with 1:1 CCl_4-ethanol and loaded with a solution of 50 mg of **2** in 0.5 mL of CCl_4. Elution with 1:1 CCl_4-ethanol yielded (+)-**2** in the early fractions, followed by (−)-**2**. A typical resolution is shown in Figure 2. Following a forerun of 47 mL which contained no **2** (by TLC), each 2-mL portion of eluate was examined polarimetrically at 436 nm (l 1 dm). The same portion was diluted to 100 mL with CCl_4, and 2 mL of this solution was further diluted to 5 mL with CCl_4. The absorbance of the resulting solution was then measured in a 1-cm cell, at 300 nm.

Racemization Kinetics. Solutions of **2** in hexachloro-1,3-butadiene (Aldrich, redistilled) were made up to 25 mL at the concentrations listed in Table II. For each kinetic run, a 25-mL sample contained in a 50-mL volumetric flask was immersed in a constant- (±0.25 °C) temperature bath maintained at 151.8, 136.9, or 120.9 °C. After 5 min was allowed for the establishment of thermal equilibrium, the first aliquot (ca. 1.5 mL) was withdrawn by syringe, and additional aliquot portions were subsequently withdrawn at regular intervals. The total number of aliquots taken over the length of the kinetic run is given in Table II as the number of data points. Each aliquot was cooled immediately after withdrawal, and its optical rotation measured in a 1-dm tube at 589, 546, and 436 nm. Rotations (α) of the first and last aliquot for each kinetic run are listed in Table II. First-order rate constants, obtained from the slope of the plot $-\ln \alpha$ vs. t, and correlation coefficients (r) are given in Table II. The infinity rotation was obtained by heating a sample with α_{589} +0.046°, α_{546} +0.056°, and α_{436} +0.109° (l 1 dm) for 1.2×10^4 s at 165.0 °C. The final rotations were indistinguishable from those of the solvent blank at all three wavelengths, indicating complete racemization within the precision of the measurements. Arrhenius activation parameters (E_a and A) given in the text were obtained from the slope and intercept of the plot $\ln k$ vs. $1/T$ ($r = 0.9993$), using a value for k at each temperature which was the average of the k's determined at the three wavelengths. Values of $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ listed in the text are obtained from the plot of $\ln k/T$ vs. $1/T$ assuming a transmission coefficient of unity in the Eyring equation.

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Supplementary Material Available: Final anisotropic thermal parameters (Table IM), bond lengths (Table IIM), and bond angles (Table IIIM) for **2** (2 pages). Ordering information is given on any current masthead page.

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(39) *Configuration* refers to the relative position or order of arrangement of atoms in space which characterizes a particular stereoisomer; it follows that all stereoisomers, regardless of type, possess distinctive configurations.[40] Expressions such as "absolute conformation"[41] are therefore subsumed under the term "absolute configuration."
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(43) Given the meaning of configuration,[39] the expression "configurational stability" simply means stability toward stereomutation, regardless of type, and applies as much to molecules possessing chiral centers, such as *trans-anti-trans-anti-trans*-perhydrotriphenylene[44a] and (D_3)-trishomocubane,[44b] as it does to molecules such as **2** or 9,24-dimethyl[2.2.2]-(4,4′,4″)triphenylmethanophane,[44c] for which the expression "conformational stability", adopted in the title of this paper, is sanctioned by conventional usage.
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