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The space group and unit cell dimensions of the tris(*p*-halophenyl)amines.

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(*Received* 11 *April* 1963)

The C–N–C bond angle in triphenylamine is of theoretical interest. Efforts to determine the structure of solid triphenylamine by X-ray diffraction studies terminated with the discovery that there are either two or four molecules in the asymmetric unit (Howells, 1950; Iveronova & Rojtburd, 1952; Howells, Lovell, Rogers & Wilson, 1954). Since it seemed possible the tris(*p*-halophenyl)amines might have unit cells with fewer molecules in the asymmetric unit, a preliminary investigation of these compounds was carried out.

The space group and unit-cell dimensions were determined from oscillation, Weissenberg, and precession photographs using Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) and Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. The fluoro, chloro, and bromo compounds are monoclinic. The iodo compound belongs to the trigonal crystal system. For the monoclinic compounds the extinctions observed were: $0k0$ with k odd and $h0l$ with h odd. For the trigonal compound there were no extinctions for the rhombohedral setting.

The densities of the fluoro and chloro compounds were measured by flotation in aqueous potassium iodide, and those of the bromo and iodo compounds in solutions of bromoform and cyclohexane. A comparison of the cell dimensions and an approximate comparison of intensities indicate that the chloro and bromo compounds are isomorphous. The fluoro compound may be isomorphous with these, but the evidence is not as conclusive.

About the time the work reported here was finished, we discovered we had overlooked the electron diffraction work of Sasaki, Kimura & Kubo (1959) on gaseous triphenylamine, in which they found a bond angle of $116 \pm 2°$. Therefore, the primary question has been answered. The trend, if any, in the C–N–C angle with changing halogen substituents would also be an interesting question, but we plan no further work on these compounds.

The authors are grateful to Professor D. Britton for his help and advice in interpreting the data and to Professor R. Walter of Haverford College who provided the compounds and raised the original question.

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Table 1. *Crystal data of tris(p-halophenyl)amines*

	$N(C_6H_4F)_3$	$N(C_6H_4Cl)_3$	$N(C_6H_4Br)_3$	$N(C_6H_4I)_3$ hexagonal	$N(C_6H_4I)_3$ rhombohedral
a	$10{\cdot}27 \pm 0{\cdot}01$ Å	$11{\cdot}25 \pm 0{\cdot}02$ Å	$11{\cdot}48 \pm 0{\cdot}01$ Å	$44{\cdot}52 \pm 0{\cdot}11$ Å	$25{\cdot}93 \pm 0{\cdot}06$ Å
b	$17{\cdot}51 \pm 0{\cdot}02$ Å	$16{\cdot}67 \pm 0{\cdot}02$ Å	$16{\cdot}74 \pm 0{\cdot}02$ Å	—	—
c	$8{\cdot}53 \pm 0{\cdot}02$ Å	$9{\cdot}21 \pm 0{\cdot}01$ Å	$9{\cdot}41 \pm 0{\cdot}01$ Å	$10{\cdot}19 \pm 0{\cdot}04$ Å	—
β	$104{\cdot}6 \pm 0{\cdot}1°$	$107{\cdot}2 \pm 0{\cdot}1°$	$107{\cdot}5 \pm 0{\cdot}1°$	—	—
α	—	—	—	—	$118° 19' \pm 30'$
U	1485 Å^3	1650 Å^3	1725 Å^3	17490 Å^3	5830 Å^3
D_m	$1{\cdot}35 \pm 0{\cdot}01$ g.cm^{-3}	$1{\cdot}41 \pm 0{\cdot}01$ g.cm^{-3}	$1{\cdot}84 \pm 0{\cdot}02$ g.cm^{-3}	$2{\cdot}14 \pm 0{\cdot}01$ g.cm^{-3}	
Z	4	4	4	36	12
D_c	$1{\cdot}352 \pm 0{\cdot}002$ g.cm^{-3}	$1{\cdot}416 \pm 0{\cdot}002$ g.cm^{-3}	$1{\cdot}867 \pm 0{\cdot}003$ g.cm^{-3}	$2{\cdot}139 \pm 0{\cdot}006$ g.cm^{-3}	
S.G.	$P2_1/a$	$P2_1/a$	$P2_1/a$	$R3$ or $R\bar{3}$	