Conformations of 1,3,5-Triaryl-1,3,5-triazacyclohexanes: Comparison of the *o*-, *m*-, and *p*-Fluorophenyl Compounds

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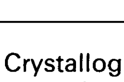
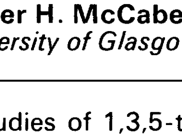
Crystallographic studies of 1,3,5-tris-(*o*-, *m*-, and *p*-fluorophenyl)-1,3,5-triazacyclohexane disclose examples of diaxial–equatorial chair conformations for 1,3,5-triaryl-1,3,5-triazacyclohexanes. The repulsion between axial aryl groups is relieved by the N–C(aryl) axial bonds being displaced outwards from ideal tetrahedral positions by 17–21°. The orientation of the equatorial aryl ring about the N–C(aryl) bond depends on the position of the F substituent. In the *p*-F compound the angle between the equatorial aromatic ring and the symmetry plane of the triazacyclohexane ring is 90° and there is maximum N lone-pair–π-orbital overlap. With increasing steric effects in the *m*- and *o*-F compounds the analogous angles are 54.7 and 22.5° and the small N lone-pair–π-orbital overlap in the *o*-F case is associated with that N atom being more pyramidal than the other N atoms in the *o*-, *m*-, and *p*-fluoro compounds.

Numerous conformational consequences of non-bonding electrons (*e.g.* the anomeric effect)[1] have been characterized in heterocyclic chemistry.[2] For the 1,3,5-trisubstituted 1,3,5-triazacyclohexanes (**1**) four chair conformations can be considered, *eee*, *eea*, *eaa*, and *aaa*, where *e* = equatorial and *a* = axial, and each of these conformations has axial interactions involving lone-pairs of electrons or substituents on the nitrogen atoms. The conformations of 1,3,5-trialkyl-1,3,5-triazacyclohexanes in solution have been investigated by dipole moment and n.m.r. methods, the former approach suggesting varying amounts of *eee*, *eea*, and *eaa* conformers[3] but subsequent ^1H and ^{13}C n.m.r. studies of the trimethyl compound (**2**) at various temperatures being interpreted in terms of a predominant *eea* conformer.[4] The tribenzyl compound (**3**) has been studied by *X*-ray crystallography at several temperatures; below *ca.* 250 K there is a single conformation *eaa* but at higher temperatures nitrogen inversion in the solid results in an overall increase in the equatorial component.[5]





(1)
(2) R = CH_3
(3) R = CH_2Ph
(4) R = Ph
(7) R = o-FC_6H_4
(8) R = m-FC_6H_4
(9) R = p-FC_6H_4

(5) R^1 = H, R^2 = Ph
(6) R = Ph, R = H

1,3,5-Triaryl-1,3,5-triazacyclohexanes have been known for some time[6] but investigation of their conformations has been confined to an *X*-ray analysis of 1,3,5-triphenyl-1,3,5-triazacyclohexane (**4**)[7] and an inconclusive n.m.r. study of that compound.[8] As in the case of the trialkyl compounds, the possible chair conformations involve axial interactions of lone-pairs of electrons and/or substituents on the nitrogen atoms. Conformational comparisons can also be made with cyclohexylbenzene where two limiting orientations of the phenyl group are possible, with the plane of the aromatic ring either perpendicular or parallel to the symmetry plane of the cyclohexane ring.[9] Force-field calculations[9] and n.m.r. measurements[10] have established that in the equatorial conformation (**5**) the phenyl group of cyclohexylbenzene favours the parallel orientation to avoid repulsive interactions between the *ortho* H atoms of the phenyl and the equatorial H atoms at C-2 and C-6 of the cyclohexane whereas in the axial conformation (**6**) the perpendicular orientation is preferred to avoid interactions between an *ortho* H atom of the phenyl and the axial H atoms at C-3 and C-5 of the cyclohexane. These descriptions are idealised, detailed study of the force-field calculations for the axial conformer showing that the preferred angle between the phenyl plane and the symmetry plane of the cyclohexane is actually *ca.* 65° rather than 90° with a variation in energy over this angular range of only *ca.* 0.2 kcal mol^{-1}. In 1,3,5-triphenyl-1,3,5-triazacyclohexane (**4**) the perpendicular orientation of a phenyl group maximises overlap between the phenyl π-orbitals and the adjacent nitrogen lone-pair orbital in both axial and equatorial conformations. In comparing (**4**) and (**5**) we note that the equatorial-perpendicular conformation of cyclohexylbenzene has been calculated to be higher in energy than the equatorial-parallel conformation by *ca.* 3.9 kcal mol^{-1}, the H(*ortho*) ··· H(2*e*,6*e*) interactions for an equatorial phenyl in (**4**) are similar to those in (**5**), and an unfavourable H(*ortho*) ··· H(1*a*) interaction of the equatorial-parallel phenyl in (**5**) is replaced by a less unfavourable H(*ortho*) ··· N(lone-pair) interaction in the equatorial-parallel rotamer of (**4**). It follows that the N lone-pair–phenyl π-orbital overlap requires a favourable energy term in excess of *ca.* 4 kcal mol^{-1} for the equatorial-perpendicular conformation to be preferred over the equatorial-parallel conformation in (**4**). Since the barrier to rotation about the N–C(aryl) bond has been estimated from spectroscopic measurements to be 5.7 kcal mol^{-1} in aniline[11] and 5.1 kcal mol^{-1} in *N*,*N*-dimethylaniline[12] but has been calculated by *ab initio* MO methods to be as low as 2.7 kcal mol^{-1} in aniline,[13] the preferred orientation of an equatorial phenyl group in (**4**) and related compounds is a matter of some interest. The crystallographic results for (**4**) show that the equatorial phenyl group in that compound adopts the perpendicular orientation in the crystal.[7]

In order to study the conformational response to varying steric requirements in 1,3,5-triaryl-1,3,5-triazacyclohexanes, we have prepared the *o*-, *m*-, and *p*-fluorophenyl compounds,

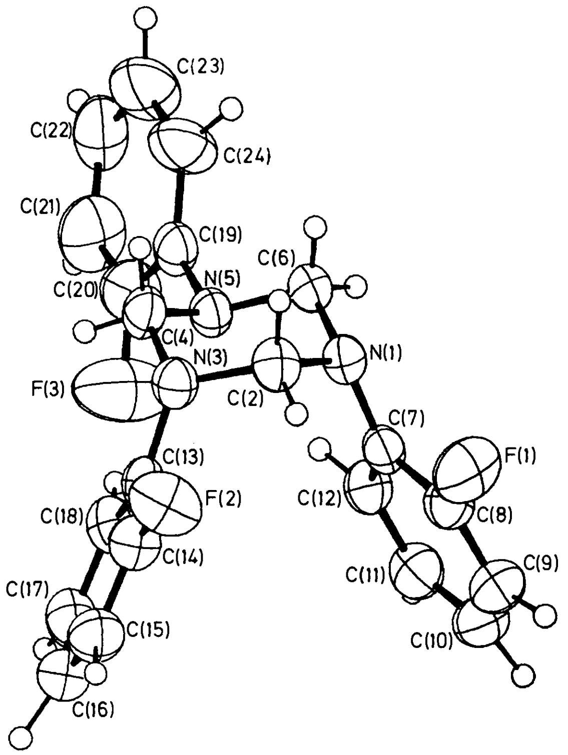


Figure 1. Molecular structure of 1,3,5-tris-(*o*-fluorophenyl)-1,3,5-triazacyclohexane (**7**). The thermal ellipsoids of the C, N, and F atoms are drawn at the 50% probability level and H atoms are represented by spheres of radius 0.1 Å.

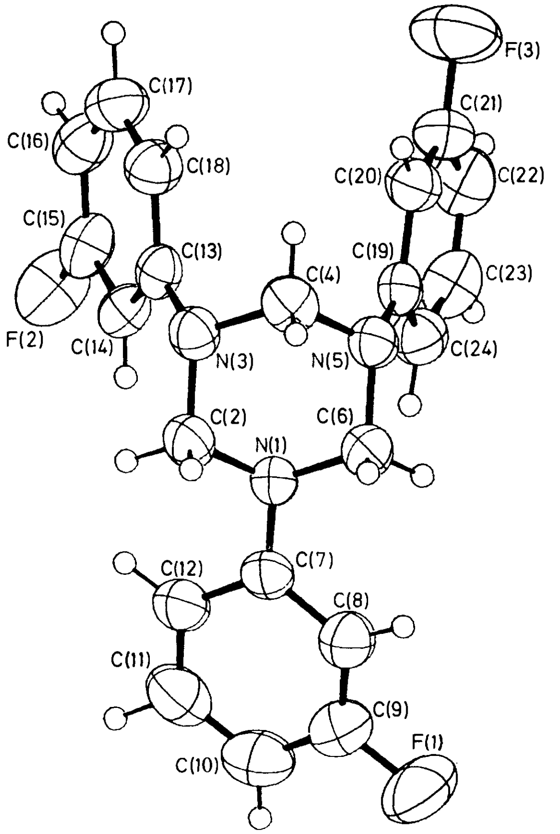


Figure 2. Molecular structure of 1,3,5-tris-(*m*-fluorophenyl)-1,3,5-triazacyclohexane (**8**). The atoms are represented as in Figure 1.

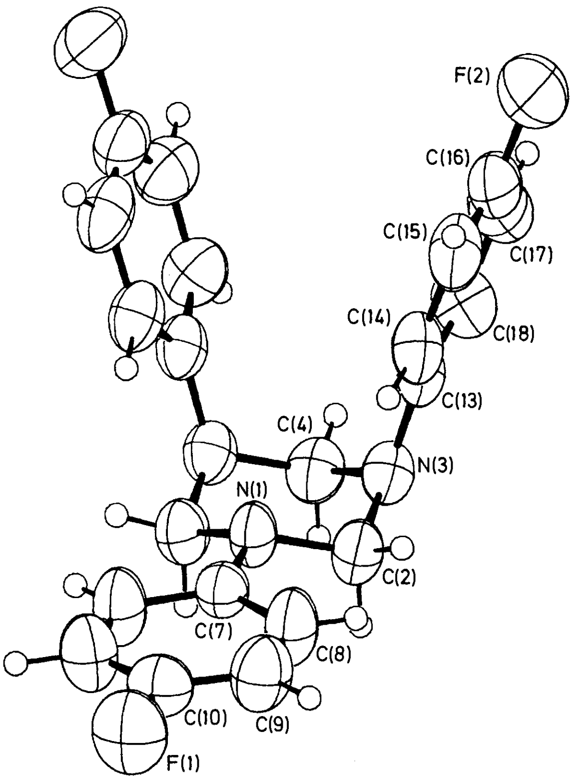


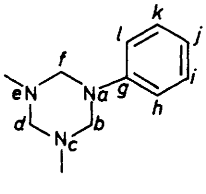
Figure 3. Molecular structure of 1,3,5-tris-(*p*-fluorophenyl)-1,3,5-triazacyclohexane (**9**). The atoms are represented as in Figure 1.

(**7**)–(**9**), and examined the molecular geometries by *X*-ray diffraction. The crystal structures were determined by direct phasing procedures [14] and the final atomic parameters obtained by full-matrix least-squares calculations. The derived molecular structures are shown in Figures 1–3. As in the case of the triphenyl compound (**4**) the molecules adopt the *eaa* conformation, with diaxial repulsion between aryl groups preferred to that between lone pairs of electrons.

Conformational parameters for (**7**)–(**9**) are listed in Table 1. The *p*-fluoro compound (**9**) has the equatorial aromatic ring in the ideal perpendicular orientation, the angle between the aromatic ring and the symmetry plane of the triazacyclohexane ring being 90°. In the *m*-fluoro compound (**8**) the appropriate angle is 54.7° and in the *o*-fluoro compound (**7**) it is 22.5°. The change in orientation of the substituted phenyl ring clearly mirrors the increasing steric requirements as the aryl group is changed from *p*- to *m*- to *o*-fluorophenyl. The effect on the axial aryl groups is less pronounced, though here also there is an indication of steric effects since the orientation angle changes from 61–65° in the *p*- (**9**) and *m*-fluorophenyl (**8**) compounds to 44–46° in the *o*-fluorophenyl compound (**7**).

The N atoms are distinctly pyramidal in character and the N–C(aryl) bonds are inclined to the appropriate CH_2–N–CH_2 planes at 32.6–48.5° (Table 1). The largest out-of-plane angle, 48.5°, is for the equatorial *o*-fluorophenyl group which is close to the parallel orientation, *i.e.* with smallest lone-pair–π-orbital overlap. For comparison, spectroscopic studies indicate that the out-of-plane angle of the N–C(aryl) bond is 37.5–42.2° in aniline,[11,15] 27.0° in *N,N*-dimethylaniline,[16] and 46.4° in *p*-fluoroaniline.[17] Since the out-of-plane angle in a tetrahedral arrangement is 54.7° the N–C(axial) bonds in (**7**)–(**9**) are splayed outwards by 17–21° from the positions in an ideal chair conformer, ameliorating the interaction between the axial aryl groups.

Table 1. Conformational details for compounds (7)–(9).



θ is angle between planes *dagj* and *aghijkl*
γ is angle between bond *a–g* and plane *fab*
ζ is angle between bond *a–g* and plane *ghijkl*

		θ(°)	γ(°)	ζ(°)
o-F	N-5 equatorial	22.5	48.5	0.9
	N-1 axial	45.7	35.9	5.4
	N-3 axial	44.1	33.7	5.6
m-F	N-1 equatorial	54.7	32.6	4.8
	N-3 axial	64.3	36.7	2.1
	N-5 axial	65.3	37.4	2.9
p-F	N-1 equatorial	90.0	36.9	4.6
	N-3 axial	61.3	37.4	2.2
	N-5 axial	61.3	37.4	2.2

In the triazacyclohexane rings the torsion angles around the C–N bonds are in the range 52.7–59.5, mean 56.5°. The CH_2–N bond lengths are 1.443–1.479, mean 1.460 Å, similar to those in the tribenzyl compound which are 1.445–1.480, mean 1.463 Å. The CH_2–N–CH_2 angles are 108.2–110.7, mean 109.7°, and the N–CH_2–N angles are 110.5–113.0, mean 111.9°.

The N atoms deviate from the phenyl planes by 0.024–0.139, mean 0.084 Å, whereas the F atoms have displacements of only 0.005–0.029, mean 0.014 Å. These departures from coplanarity correspond to out-of-plane angles of 0.2–1.2, mean 0.6°, for the C(aryl)–F bonds and 0.9–5.6, mean 3.4°, for the C(aryl)–N bonds. The molecular geometry of aniline has recently been computed by *ab initio* gradient MO methods and for the equilibrium conformation in which the dihedral angle between the N lone-pair orbital and the aromatic π-orbitals is 0° the C(aryl)–N bond was estimated to be inclined at 2.4° to the aromatic plane, whereas for the higher-energy conformation in which the dihedral angle is 90° the N atom does not deviate from the aromatic plane.[13] In agreement with this, the minimum out-of-plane angle for the C(aryl)–N bonds in (7)–(9) is for the equatorial-parallel bond in the *o*-fluoro derivative, where the dihedral angle between the N lone-pair orbital and the aromatic π-orbitals is 67.5°; this involves, concomitantly, the most pyramidal of the N atoms (Table 1) and the one with the longest C(aryl)–bond, 1.427 Å. The *ab initio* calculations for fluorobenzene indicate no departure from planarity.[18]

In substituted benzene rings, the ring angle at a substituent is related to the electron-donating or -withdrawing σ-character of the substituent;[19] the phenyl ring angle at F is expected to be greater than 120° (observed 121.2–123.8, mean 122.8°) and that at N to be less than 120° (observed 115.5–117.8, mean 116.9°).

In the solution state, facile conformational inversion of (7)–(9) results in averaging of the ^1H n.m.r. signals of the axial and equatorial CH_2 hydrogen atoms, which appear as a narrow singlet in all three cases. In low-temperature spectra of (9) in CD_2Cl_2–CF_2Cl_2–$(CD_3)_2CO$ (1:1:1), marked broadening of both aryl and methylene resonances was observed as the temperature was taken below −70° but the coalescence temperature for the methylene signal had not been reached by −135° [*cf.* (4)].[8]

Experimental

Formalin was of concentration 37–39% (w/w) and ethanol absolute (99.8% v/v). Benzene was dried over sodium wire. Mass spectra were run on a VG upgraded Kratos MS12 instrument and i.r. spectra of chloroform solutions on a Perkin-Elmer 580 spectrophotometer. N.m.r. spectra were recorded at 90 MHz on a Perkin-Elmer R32 spectrometer for solutions in deuteriochloroform with tetramethylsilane as internal reference. Quoted yields are not regarded as optimum.

1,3,5-*Tris*-(o-*fluorophenyl*)-1,3,5-*triazacyclohexane* (7).—*o*-Fluoroaniline (2.32 g, 20 mmol) was stirred overnight at ambient temperature with water (10 cm^3), potassium hydroxide (1.15 g, 20.5 mmol) and an excess of formalin (6 cm^3). The mixture was extracted with ether, the ether layer dried (Na_2SO_4) and evaporated under suction to yield (7) as an oil which solidified on standing. Recrystallisation from light petroleum (b.p. 60–80 °C) gave needles (1.99 g, 81%), m.p. 176–178 °C (Found: C, 68.3; H, 4.8; F, 15.4; N, 11.2. $C_{21}H_{18}F_3N_3$ requires C, 68.3; H, 4.9; F, 15.4; N, 11.4%); *m/z* 369 (*M*), 246 ($M - C_7H_6NF$), and 123 (C_7H_6NF, base peak); $\nu_{max.}$ 3 070, 3 015, 2 830, 1 501, 1 239, 1 225, 1 200, 1 042, 736, and 668 cm^{-1}; δ_H 4.92 (6 H, s, CH_2) and 6.8–7.5 (12 H, m, Ar).

1,3,5-*Tris*-(m-*fluorophenyl*)-1,3,5-*triazacyclohexane* (8).—*m*-Fluoroaniline (2.23 g, 20 mmol) was stirred and heated (bath temperature slowly raised from 90 to 102 °C) with paraformaldehyde (0.63 g, 21 mmol) in anhydrous benzene (30 cm^3) with azeotropic removal of water, using a Dean and Stark apparatus. The remaining benzene was removed under reduced pressure and the solid residue recrystallised from hexane to yield (8) as leaflets (1.94 g, 79%), m.p. 84–85 °C (Found: C, 68.2; H, 4.8; N, 11.4%); *m/z* 369, 246, and 123 (base peak); $\nu_{max.}$ 3 025, 2 830, 1 610, 1 585, 1 487, 1 256, 1 198, 1 140, 985, and 687 cm^{-1}; δ_H 4.91 (6 H, s, CH_2) and 6.5–7.4 (12 H, m, Ar).

1,3,5-*Tris*-(p-*fluorophenyl*)-1,3,5-*triazacyclohexane* (9).—Formalin (10 cm^3) was added with stirring to a solution of *p*-fluoroaniline (5.56 g, 50 mmol) in EtOH (20 cm^3). The precipitate (9) (4.27 g, 69%) was recrystallised from ether as needles or prisms, m.p. 161–162 °C (Found: C, 68.25; H, 4.8; N, 11.3; F, 15.4%); *m/z* 123 ($FC_6H_4NCH_2$) and 95 (C_6H_4F, base peak); $\nu_{max.}$ 3 030, 2 835, 1 510, 1 238, 1 225, 1 161, 1 104, 829, and 622 cm^{-1}; δ_H 4.76 (6 H, s, CH_2), 6.93 (*ca.* 6 H, d, *J* 7 Hz, Ar), and 6.97 (*ca.* 6 H, d, *J* 7 Hz, Ar).

Crystal Data.—1,3,5-Tris-(*o*-fluorophenyl)-1,3,5-triazacyclohexane (7), $C_{21}H_{18}F_3N_3$, $M = 369.42$, monoclinic, $a = 6.683(3)$, $b = 20.728(2)$, $c = 13.739(2)$ Å, $\beta = 112.79(2)°$, $V = 1\,755$ Å^3, $D_c = 1.40$ g cm^{-3}, $Z = 4$, $F(000) = 768$, $\mu(Cu\text{-}K_\alpha) = 9.2$ cm^{-1}, space group $P2_1/c$ (No. 14).

1,3,5-Tris-(*m*-fluorophenyl)-1,3,5-triazacyclohexane (8), $C_{21}H_{18}F_3N_3$, $M = 369.42$, orthorhombic, $a = 13.629(2)$, $b = 12.798(3)$, $c = 20.586(2)$ Å, $V = 3\,591$ Å^3, $D_c = 1.37$ g cm^{-3}, $Z = 8$, $F(000) = 1\,536$, $\mu(Mo\text{-}K_\alpha) = 1.13$ cm^{-1}, space group *Pbca* (No. 61).

1,3,5-Tris-(*p*-fluorophenyl)-1,3,5-triazacyclohexane (9), $C_{21}H_{18}F_3N_3$, $M = 369.42$, orthorhombic, $a = 14.412(2)$, $b = 20.395(2)$, $c = 12.100(2)$ Å, $V = 3\,557$ Å^3, $D_c = 1.38$ g cm^{-3}, $Z = 8$, $F(000) = 1\,536$, $\mu(Cu\text{-}K_\alpha) = 9.0$ cm^{-1}, space group *Cmca* (No. 64).

Crystallographic Measurements.—Cell dimensions were derived from least-squares analysis of the setting angles of 25 reflections measured on an Enraf–Nonius CAD4 diffractometer. For compound (7), 4 661 reflections were surveyed in the range $\theta < 72°$ (Cu-K_α radiation) and after merging 1 722 observations to get 663 independent intensities (merging $R = 0.050$), 2 945

Table 2. Fractional atomic co-ordinates for 1,3,5-tris-(*o*-fluorophenyl)-1,3,5-triazacyclohexane (**7**) (e.s.d.s in parentheses).

Atom	x	y	z
N(1)	0.400 3(2)	0.048 9(1)	0.351 2(1)
C(2)	0.411 5(3)	0.072 3(1)	0.252 5(1)
N(3)	0.240 5(3)	0.045 8(1)	0.158 3(1)
C(4)	0.236 7(4)	−0.023 7(1)	0.163 6(1)
N(5)	0.212 5(2)	−0.046 2(1)	0.260 6(1)
C(6)	0.395 2(3)	−0.020 9(1)	0.352 1(1)
C(7)	0.261 7(3)	0.081 8(1)	0.390 2(1)
C(8)	0.313 0(3)	0.144 7(1)	0.427 4(1)
C(9)	0.199 2(4)	0.178 3(1)	0.475 4(2)
C(10)	0.023 2(4)	0.149 5(1)	0.487 1(2)
C(11)	−0.033 8(4)	0.087 6(1)	0.450 3(2)
C(12)	0.081 9(3)	0.054 5(1)	0.402 1(1)
C(13)	0.038 7(3)	0.078 4(1)	0.115 4(1)
C(14)	0.028 9(3)	0.138 8(1)	0.068 9(1)
C(15)	−0.159 5(4)	0.171 5(1)	0.016 4(2)
C(16)	−0.354 0(4)	0.144 2(1)	0.009 3(2)
C(17)	−0.351 9(4)	0.084 4(1)	0.054 8(2)
C(18)	−0.159 3(3)	0.052 4(1)	0.107 5(1)
C(19)	0.189 5(3)	−0.114 7(1)	0.261 4(1)
C(20)	−0.012 7(4)	−0.140 5(1)	0.238 3(2)
C(21)	−0.050 4(6)	−0.206 8(1)	0.234 6(2)
C(22)	0.120 6(6)	−0.247 7(1)	0.257 2(2)
C(23)	0.322 5(6)	−0.224 3(1)	0.281 3(3)
C(24)	0.359 8(5)	−0.157 7(1)	0.283 3(2)
F(1)	0.486 2(2)	0.173 5(1)	0.417 5(1)
F(2)	0.219 4(2)	0.165 7(1)	0.074 5(1)
F(3)	−0.182 1(3)	−0.100 2(1)	0.217 2(2)

Table 3. Fractional atomic co-ordinates for 1,3,5-tris-(*m*-fluorophenyl)-1,3,5-triazacyclohexane (**8**) (e.s.d.s in parentheses).

Atom	x	y	z
N(1)	0.735 76(14)	0.227 86(18)	0.920 09(9)
C(2)	0.814 9(2)	0.301 8(3)	0.936 9(1)
N(3)	0.804 95(15)	0.340 48(16)	1.002 41(10)
C(4)	0.708 2(2)	0.386 7(2)	1.011 4(2)
N(5)	0.629 48(15)	0.314 55(16)	0.995 48(9)
C(6)	0.640 3(2)	0.278 4(3)	0.929 1(1)
C(7)	0.747 93(19)	0.159 99(22)	0.867 49(11)
C(8)	0.671 8(2)	0.139 2(3)	0.824 4(1)
C(9)	0.683 8(3)	0.065 7(3)	0.777 0(1)
C(10)	0.768 4(3)	0.012 1(3)	0.767 9(2)
C(11)	0.843 5(3)	0.034 4(3)	0.809 3(2)
C(12)	0.835 5(2)	0.106 7(3)	0.858 0(1)
C(13)	0.840 00(17)	0.278 30(19)	1.054 34(12)
C(14)	0.878 71(18)	0.180 21(21)	1.045 47(14)
C(15)	0.915 32(19)	0.126 95(20)	1.098 11(14)
C(16)	0.914 7(2)	0.165 9(3)	1.159 7(1)
C(17)	0.876 5(2)	0.263 0(3)	1.168 4(1)
C(18)	0.840 4(2)	0.319 5(2)	1.117 1(1)
C(19)	0.604 08(17)	0.238 16(21)	1.042 46(12)
C(20)	0.586 7(2)	0.268 8(3)	1.106 3(1)
C(21)	0.558 3(2)	0.195 6(3)	1.150 5(1)
C(22)	0.543 9(2)	0.092 8(3)	1.135 5(2)
C(23)	0.560 3(2)	0.063 1(3)	1.072 8(2)
C(24)	0.590 6(2)	0.134 2(2)	1.027 1(2)
F(1)	0.608 57(16)	0.048 76(18)	0.736 40(11)
F(2)	0.953 73(13)	0.030 46(13)	1.087 21(9)
F(3)	0.542 40(17)	0.227 03(17)	1.212 03(8)

Table 4. Fractional atomic co-ordinates for 1,3,5-tris-(*p*-fluorophenyl)-1,3,5-triazacyclohexane (**9**) (e.s.d.s in parentheses).

Atom	x	y	z
N(1)	0.500 0	0.153 5(1)	0.490 2(2)
N(3)	0.584 51(11)	0.228 30(8)	0.372 29(13)
C(2)	0.583 40(14)	0.163 96(11)	0.421 59(19)
C(4)	0.500 0	0.238 2(2)	0.306 9(2)
C(7)	0.500 0	0.099 6(1)	0.562 9(2)
C(8)	0.581 50(16)	0.072 20(13)	0.603 22(22)
C(9)	0.581 84(18)	0.023 11(13)	0.680 56(21)
C(10)	0.500 0	−0.000 6(2)	0.718 3(2)
C(13)	0.613 74(12)	0.281 85(10)	0.439 27(16)
C(14)	0.633 52(14)	0.275 71(12)	0.550 10(18)
C(15)	0.666 26(15)	0.329 02(15)	0.610 44(20)
C(16)	0.677 45(15)	0.387 33(13)	0.559 44(23)
C(17)	0.658 85(18)	0.395 59(14)	0.450 03(25)
C(18)	0.627 91(18)	0.342 44(11)	0.391 01(20)
F(1)	0.500 0	−0.049 4(1)	0.795 0(2)
F(2)	0.710 23(11)	0.439 29(8)	0.619 06(14)

independent reflections satisfied the criterion $I > 2.5\sigma(I)$. For compound (**8**), 3 195 reflections were surveyed in the range $\theta < 30°$ (Mo-K_α radiation) and 1 643 satisfied the criterion $I > 2.5\sigma(I)$. For compound (**9**), 1 972 reflections were surveyed in the range $\theta < 72°$ (Cu-K_α radiation) and 1 294 satisfied the criterion $I > 2.5\sigma(I)$.

Structure Analyses.—The crystal structures were elucidated by the direct phasing program MITHRIL.[14] After preliminary least-squares adjustment of the co-ordinates and anisotropic thermal parameters of the C, N, and F atoms, the H atoms were located in difference electron density distributions and subsequently included in the least-squares calculations with isotropic thermal parameters. The weighting scheme used was $w = 1/\sigma^2(|F|)$. The calculations converged at $R = 0.046$, $R_w = 0.072$ for compound (**7**), $R = 0.036$, $R_w = 0.042$ for compound (**8**), and $R = 0.051$, $R_w = 0.060$ for compound (**9**). Fourier, least-squares, geometry, and ORTEP calculations were performed with the GX package of programs.[20]

Atomic co-ordinates are listed in Tables 2–4. Full details of the molecular geometries, together with thermal parameters and hydrogen atom positions have been deposited with the Cambridge Crystallographic Data Centre.*

Acknowledgements

We thank the Direction de la Formation à l'Etranger du Ministère de l'Enseignement Supérieur de la République Algérienne for a research scholarship to A. B.

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Received 9*th June* 1988; *Paper* 8/02310G