Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *of* 1,2diMeαNeu5Ac

	D—H	H···A	D···A	D—H···A	Symmetry operation*
O(4)—H(14)···O(8)	0·83 (2)	2·04 (2)	2·825 (2)	158 (2)	545·3
O(9)—H(19)···O(7)	0·81 (2)	2·01 (2)	2·787 (2)	160 (2)	655·3
N(5)—H(25)···O(9)	0·87 (2)	1·93 (2)	2·793 (2)	172 (2)	455·1
O(7)—H(17)···O(12)	0·84 (2)	1·88 (2)	2·704 (2)	167 (2)	555·1
O(8)—H(18)···O(1)	0·85 (2)	1·99 (2)	2·832 (2)	170 (2)	555·1

* The symmetry operation is performed on the acceptors (*A*). The first three digits specify the lattice translations. The last digit indicates one of the following symmetry operations: (1) x, y, z; (2) $\frac{1}{2}+x, \frac{1}{2}-y, -z$; (3) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (4) $\frac{1}{2}-x, -y, \frac{1}{2}+z$ (*e.g.* 545·3 is $-b$ from 555·3).

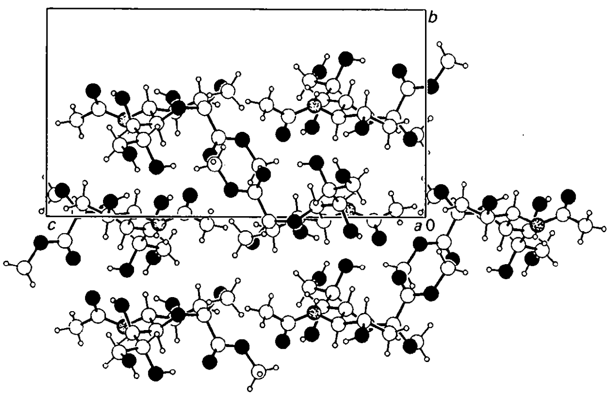

Fig. 2. View of the structure down the *a* axis. The C, O, N and H atoms are represented by white, black, dotted and small spheres, respectively.

NMR data (Czarniecki & Thornton, 1977) on α and β forms of Neu5Ac in aqueous solution, low mobility was found around the C(6)—C(7) and C(7)—C(8) bonds. The persistence of this particular glycerol side-chain conformation in crystals is in agreement with these findings.

The hydrogen-bonding geometries in the crystal structure of 1,2diMeαNeu5Ac are listed in Table 3. Every molecule is surrounded by six hydrogen-bonded neighbours. A two-dimensional network is formed by hydrogen bonds in the [100] and [110] directions. The contacts in the [001] direction are hydrophobic in nature. Fig. 2 gives a view of the structure down **a**.

The authors thank Dr P. van der Sluis for growing the crystals and Dr J. P. Kamerling for supplying the material.

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Conformational Study of 1,3,5-Tris(*o*-chlorophenyl)-1,3,5-triazacyclohexane and 1,3,5-Tris(*p*-chlorophenyl)-1,3,5-triazacyclohexane

BY AHCENE BOUCHEMMA, PETER H. MCCABE AND GEORGE A. SIM

Chemistry Department, University of Glasgow, Glasgow G12 8QQ, Scotland

(*Received* 12 *May* 1989; *accepted* 23 *June* 1989)

Abstract. $C_{21}H_{18}Cl_3N_3$, $M_r = 418·80$. *o*-Chlorophenyl compound, orthorhombic, *Pnma*, $a = 20·899$ (4), $b = 12·466$ (3), $c = 7·372$ (1) Å, $V = 1921$ (1) Å^3, $Z = 4$, $D_x = 1·45$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·49$ mm^{-1}, $F(000) = 864$, $T = 293$ K, $R = 0·040$ for 1581 independent observed reflections. *p*-Chloro-

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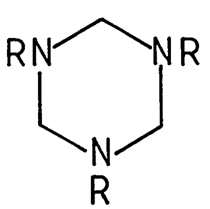
phenyl compound, orthorhombic, *Pbcm*, $a = 5{\cdot}689\,(2)$, $b = 21{\cdot}874\,(3)$, $c = 15{\cdot}789\,(3)$ Å, $V = 1965\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}42$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 4{\cdot}3$ mm^{-1}, $F(000) = 864$, $T = 293$ K, $R = 0{\cdot}053$ for 1190 independent observed reflections. Triazacyclohexane rings adopt chair conformations with equatorial–diaxial orientation of the aryl groups. The repulsion between axial aryl groups is relieved by the N—C(aryl) axial bonds being displaced outwards from ideal tetrahedral positions by 19–22°. In the *p*-Cl compound, the angle between the plane of the equatorial aromatic ring and the symmetry plane of the molecule is 90°, there is maximum N-lone-pair/π-orbital overlap, and the N—C(aryl) bond length is 1·405 (8) Å. In the *o*-Cl compound, the analogous angle for the equatorial substituent is 0°, there is no lone-pair/π-orbital overlap, the N atom is appreciably more pyramidal than the other N atoms in these molecules, and the N—C(aryl) equatorial bond length is 1·433 (4) Å. The torsion angles around the N—C bonds in the triazacyclohexane ring are 53·1–56·7 (2)° (*o*-Cl) and 55·6–58·9 (5)° (*p*-Cl).

Introduction. Heterocyclic compounds offer a variety of possibilities for the study of the conformational effects of non-bonding electrons (Riddell, 1980; Crabb & Katritzky, 1984). 1,3,5-Triaryl-1,3,5-triazacyclohexanes (I) were first prepared many years ago (Wellington & Tollens, 1885) but their conformations have only recently been investigated (Farmer & Hamer, 1968; Giumanini, Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985; Bouchemma, McCabe & Sim, 1989). If the heterocyclic nucleus adopts a chair conformation, four patterns of substituent orientation have to be considered, *eee*, *eea*, *eaa* and *aaa*, where *e* = equatorial and *a* = axial, and each of these conformers has axial interactions involving the lone pairs of electrons and/or the substituents on the N atoms. The triphenyl compound (Giumanini, Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985) and the *o*-, *m*- and *p*-fluorophenyl compounds (Bouchemma, McCabe & Sim, 1989) all exhibit the *eaa* chair conformation in the solid state.



(I)

In the study of the *o*-, *m*- and *p*-fluorophenyl compounds, we examined the relationship between the inclination of the equatorial aryl ring around the N—C(aryl) bond and the position of the F substituent. In the *p*-F compound the equatorial aromatic ring is perpendicular to the symmetry plane of the triazacyclohexane, the N-lone-pair/π-orbital dihedral angle is 0° and there is maximum lone-pair/π-orbital overlap. With increased steric effects in the *m*-F and *o*-F compounds the equatorial aromatic ring is forced away from this ideal orientation to avoid repulsive interactions with the equatorial H atoms of the C atoms adjacent to nitrogen in the triazacyclohexane ring. The N-lone-pair/π-orbital dihedral angle for the equatorial aromatic group in the *o*-F compound is *ca* 69°, there is little lone-pair/π-orbital overlap and the N atom is more pyramidal than the other N atoms in these compounds (Bouchemma, McCabe & Sim, 1989).

The *o*-chlorophenyl and *p*-chlorophenyl compounds were investigated to obtain additional information about the conformational consequences of substituents in the *o*-position of the aryl rings in 1,3,5-triaryl-1,3,5-triazacyclohexanes.

Experimental. 1,3,5-Tris(*o*-chlorophenyl)-1,3,5-triazacyclohexane [(I), $R = o$-ClC_6H_4] was prepared in 60% yield by a reported procedure (Pernyeszi, Bagi, Nagy, Gesztelyi Nagy, Sugar, Nagy, Nadasy & Szanto, 1985) except that the formalin used was 38% *w*/*w*. The product crystallized from benzene as needles, m.p. 497–498 K (Reichert hot stage), 483–484 K (Gallenkamp) (lit. m.p. 683 K) (Found: C, 60·31; H, 4·23; N, 10·06. $C_{21}H_{18}Cl_3N_3$ requires C, 60·21; H, 4·33; N, 10·03%); *m*/*z* 282 (0·6), 280 (3·8), 278 (5·8) ($\frac{2}{3}M$), 141 (21), 139 (100) ($\frac{1}{3}M$), 113 (4·5) and 111 (14%) (C_6H_4Cl) (results in parentheses give the abundance of each ion relative to that of the major ion); ν_{max}(KBr) 3060, 2905, 2825, 1588, 1486, 1478, 1389, 1217, 940 and 754 cm^{-1}; δ($CDCl_3$, 90 MHz) 4·7 (*s*, 6H; CH_2) and 6·7–7·2 (*m*, 12H; Ar). 1,3,5-Tris(*p*-chlorophenyl)-1,3,5-triazacyclohexane [(I), $R = p$-ClC_6H_4] was prepared in 69% yield, following a reported procedure (Ingold, 1924) with minor modification, and crystallized from 1:1 ether–petroleum spirit (b.p. 333–353 K) with m.p. 414·5–415·5 K (lit. 415 K); *m*/*z* 141 (32), 139 (100) ($\frac{1}{3}M$), 113 (22) and 111 (67%); ν_{max}($CHCl_3$) 3020, 1596, 1496, 1097 and 825 cm^{-1}; δ($CDCl_3$, 90 MHz) 4·78 (*s*, 6H, CH_2), 6·86 (*d*, J = 9Hz, 6H; Ar) and 7·15 (*d*, J = 9Hz, 6H; Ar).

o-Chlorophenyl compound. Crystal dimensions 0·15 × 0·3 × 0·6 mm. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, generator settings 50 kV, 20 mA. Cell dimensions from setting angles of 25 reflections with θ 12–18°; 2676 reflections surveyed in range θ 1·5–28·0°; h 0→7, k 0→16, l 0→9; scan width $1{\cdot}0° + 0{\cdot}25°\tan\theta$; max. scan time 120 s; 1581 independent reflections with $I > 2{\cdot}5\sigma(I)$.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å²) *for* (*A*) 1,3,5-*tris*(*o*-*chlorophenyl*)-1,3,5-*triazacyclohexane and* (*B*) 1,3,5-*tris*(*p*-*chlorophenyl*)-1,3,5-*triazacyclohexane*

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

	x	y	z	U_{eq}
A				
Cl(1)	0·33271 (3)	0·06473 (7)	0·63278 (9)	0·070
Cl(2)	0·59633 (5)	0·25000	0·03487 (12)	0·068
N(1)	0·46183 (7)	0·15230 (13)	0·53522 (22)	0·037
C(2)	0·53073 (10)	0·15360 (18)	0·51659 (31)	0·040
N(3)	0·55336 (11)	0·25000	0·42041 (32)	0·034
C(6)	0·43922 (15)	0·25000	0·62289 (41)	0·042
C(7)	0·42570 (9)	0·11183 (16)	0·38794 (26)	0·036
C(8)	0·36517 (10)	0·06796 (17)	0·41590 (30)	0·043
C(9)	0·33060 (12)	0·02130 (21)	0·27892 (38)	0·055
C(10)	0·35576 (14)	0·01615 (22)	0·10752 (39)	0·059
C(11)	0·41524 (13)	0·05713 (20)	0·07446 (37)	0·056
C(12)	0·44943 (11)	0·10464 (18)	0·21181 (30)	0·045
C(13)	0·62138 (14)	0·25000	0·39540 (43)	0·040
C(14)	0·64724 (16)	0·25000	0·22164 (47)	0·048
C(15)	0·71252 (19)	0·25000	0·19270 (67)	0·064
C(16)	0·75347 (18)	0·25000	0·33737 (75)	0·069
C(17)	0·72955 (17)	0·25000	0·50976 (71)	0·066
C(18)	0·66440 (17)	0·25000	0·53873 (58)	0·056
B				
N(1)	0·7440 (7)	−0·0194 (2)	0·1737 (2)	0·070
C(2)	0·6727 (10)	−0·0826 (2)	0·1739 (3)	0·071
N(3)	0·5309 (9)	−0·0963 (2)	0·2500	0·062
C(6)	0·8754 (12)	−0·0049 (4)	0·2500	0·075
C(7)	0·5870 (7)	0·0239 (2)	0·1399 (2)	0·061
C(8)	0·3711 (8)	0·0090 (2)	0·1066 (3)	0·065
C(9)	0·2337 (9)	0·0518 (2)	0·0672 (3)	0·071
C(10)	0·3041 (9)	0·1107 (2)	0·0602 (2)	0·070
C(11)	0·5123 (11)	0·1279 (2)	0·0951 (4)	0·084
C(12)	0·6520 (10)	0·0851 (3)	0·1324 (4)	0·085
C(13)	0·3922 (11)	−0·1494 (2)	0·2500	0·058
C(14)	0·3132 (11)	−0·1757 (2)	0·1761 (3)	0·088
C(15)	0·1549 (11)	−0·2234 (3)	0·1763 (3)	0·094
C(16)	0·0789 (10)	−0·2475 (3)	0·2500	0·067
Cl(1)	0·1320 (3)	0·1652 (1)	0·0095 (1)	0·103
Cl(2)	−0·1236 (4)	−0·3077 (1)	0·2500	0·098

p-Chlorophenyl compound. Crystal dimensions 0·05 × 0·2 × 0·4 mm. Enraf–Nonius CAD-4 diffractometer, Cu $K\alpha$ radiation, generator settings 43 kV, 26 mA. Cell dimensions from setting angles of 25 reflections with θ 16–21°, 2197 reflections surveyed in range θ 2·0–72·0°; h 0→6, k 0→19, l 0→26; scan width 1·2° + 0·2° tan θ; max. scan time 120 s; 1190 independent reflections with $I > 2{\cdot}5\sigma(I)$. Two reference reflections monitored periodically showed no significant variation in intensity. Corrections applied for Lorentz–polarization effects, assuming ideally imperfect monochromator crystals. Both structures determined by direct phasing using *MITHRIL* (Gilmore, 1984). H atoms located in difference Fourier syntheses. Full-matrix least-squares calculations on F with anisotropic thermal parameters for C, N and Cl atoms and isotropic for H atoms. Convergence at $R = 0{\cdot}040$, $wR = 0{\cdot}049$, $S = 2{\cdot}11$ for 178 parameters, $\Delta/\sigma < 0{\cdot}3$, $w = 1/\sigma^2(|F_o|)$, final $\Delta\rho$ max. 0·20, min. −0·31 e Å^{-3} for the *o*-chlorophenyl compound. Convergence at $R = 0{\cdot}053$, $wR = 0{\cdot}073$, $S = 2{\cdot}98$ for 169 parameters, $\Delta/\sigma < 0{\cdot}2$, $w = 1/\sigma^2(|F_o|)$, final $\Delta\rho$ max. 0·18, min. −0·36 e Å^{-3} for the *p*-chlorophenyl compound. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations on an SEL 32/27 computer with the *GX* system of programs (Mallinson & Muir, 1985).

Table 2. *Interatomic distances* (Å) *and angles* (°) *for* 1,3,5-*tris*(*o*-*chlorophenyl*)-1,3,5-*triazacyclohexane* (*column A*) *and* 1,3,5-*tris*(*p*-*chlorophenyl*)-1,3,5-*triazacyclohexane* (*column B*)

	A	*B*
Cl(1)—C(8)	1·737 (3)	
Cl(2)—C(14)	1·740 (4)	
Cl(1)—C(10)		1·736 (5)
Cl(2)—C(16)		1·749 (7)
N(1)—C(2)	1·447 (3)	1·440 (6)
N(1)—C(6)	1·458 (3)	1·454 (8)
N(1)—C(7)	1·415 (3)	1·408 (6)
N(3)—C(2)	1·473 (3)	1·478 (7)
N(3)—C(13)	1·433 (4)	1·405 (8)
C(7)—C(8)	1·393 (3)	1·376 (7)
C(7)—C(12)	1·393 (3)	1·394 (8)
C(8)—C(9)	1·371 (4)	1·369 (7)
C(9)—C(10)	1·370 (4)	1·355 (7)
C(10)—C(11)	1·366 (4)	1·359 (8)
C(11)—C(12)	1·374 (4)	1·362 (9)
C(13)—C(14)	1·390 (5)	1·376 (7)
C(14)—C(15)	1·381 (6)	1·378 (9)
C(15)—C(16)	1·367 (7)	1·348 (7)
C(16)—C(17)	1·366 (8)	
C(17)—C(18)	1·378 (6)	
C(18)—C(13)	1·387 (6)	
C(2)—N(1)—C(6)	110·8 (2)	110·6 (5)
C(2)—N(1)—C(7)	117·5 (2)	118·0 (4)
C(6)—N(1)—C(7)	117·7 (2)	119·5 (5)
N(1)—C(2)—N(3)	112·0 (2)	110·5 (4)
C(2)—N(3)—C(4)	109·3 (3)	108·7 (5)
C(2)—N(3)—C(13)	112·3 (2)	118·3 (4)
N(1)—C(6)—N(5)	113·4 (3)	112·0 (6)
N(1)—C(7)—C(8)	120·7 (2)	123·5 (4)
N(1)—C(7)—C(12)	123·2 (2)	120·8 (5)
C(8)—C(7)—C(12)	115·8 (2)	115·6 (5)
C(7)—C(8)—C(9)	122·4 (3)	121·4 (5)
Cl(1)—C(8)—C(7)	120·0 (2)	
Cl(1)—C(8)—C(9)	117·5 (2)	
C(8)—C(9)—C(10)	119·8 (3)	121·3 (5)
C(9)—C(10)—C(11)	119·8 (3)	119·2 (5)
C(9)—C(10)—Cl(1)		121·6 (4)
C(11)—C(10)—Cl(1)		119·2 (4)
C(10)—C(11)—C(12)	120·2 (3)	119·6 (5)
C(7)—C(12)—C(11)	122·0 (3)	122·8 (6)
N(3)—C(13)—C(14)	120·3 (3)	121·9 (4)
N(3)—C(13)—C(18)	123·0 (3)	121·9 (4)
C(14)—C(13)—C(18)	116·7 (3)	116·0 (5)
C(13)—C(14)—C(15)	121·8 (4)	121·8 (5)
Cl(2)—C(14)—C(13)	119·4 (3)	
Cl(2)—C(14)—C(15)	118·8 (4)	
C(14)—C(15)—C(16)	119·9 (5)	120·6 (5)
C(15)—C(16)—C(17)	119·8 (4)	119·2 (6)
C(15)—C(16)—Cl(2)		120·4 (4)
C(16)—C(17)—C(18)	120·4 (5)	
C(13)—C(18)—C(17)	121·5 (4)	

Discussion. Atomic coordinates and molecular dimensions are listed in Tables 1 and 2.* Figs. 1 and 2, drawn with *ORTEP* (Johnson, 1965), illustrate the molecular structures.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52373 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Both molecules adopt the *eaa* conformation in the solid state, as do the phenyl (Giumanini, Verardo, Randaccio, Bresciani-Pahor & Traldi, 1985) and the *o*-, *m*- and *p*-fluorophenyl (Bouchemma, McCabe & Sim, 1989) compounds, with diaxial repulsion between aryl groups preferred to that between lone pairs of electrons.

Conformational parameters for the *o*- and *p*-chlorophenyl compounds are listed in Table 3. In the *p*-chlorophenyl compound the angle between the equatorial aromatic ring and the symmetry plane of the triazacyclohexane is 90° and in this conformation there is maximum overlap between the N(3) lone pair and the π orbitals of the aromatic ring. In the *o*-chlorophenyl compound, in contrast, the equatorial aromatic ring lies in the symmetry plane of the molecule so that there is no overlap between the N(3) lone pair and the π orbitals of the aromatic ring.

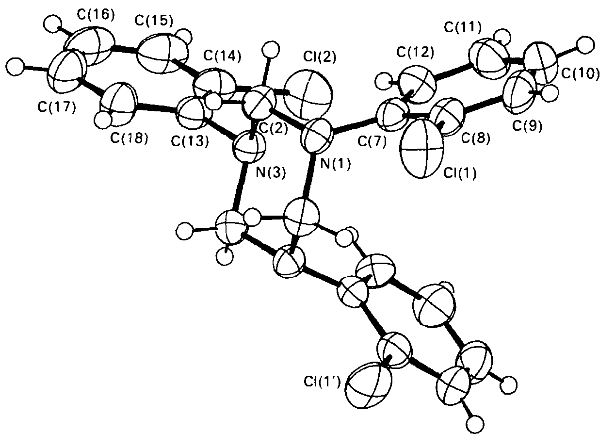


Fig. 1. Molecular structure and atomic numbering for 1,3,5-tris(*o*-chlorophenyl)-1,3,5-triazacyclohexane. The thermal ellipsoids of the C and N atoms are drawn at the 50% probability level and the H atoms are represented by spheres of radius 0·1 Å.

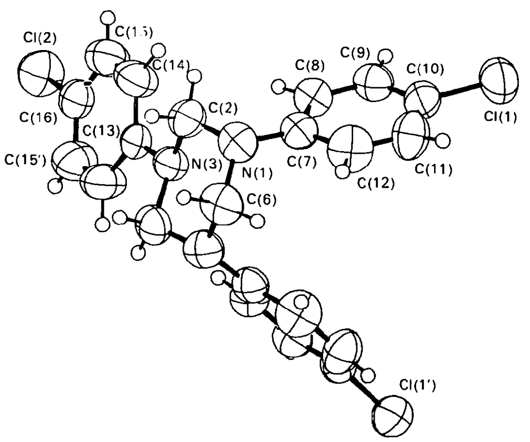
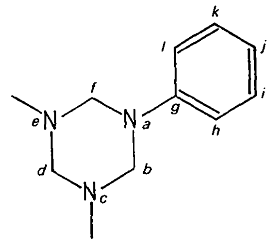


Fig. 2. Molecular structure and atomic numbering for 1,3,5-tris(*p*-chlorophenyl)-1,3,5-triazacyclohexane. Atoms are represented as in Fig. 1.

Table 3. *Conformational details*



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
p-Cl	N(3) equatorial	90·0	35·5 (5)	6·5 (5)
	N(1) axial	68·1 (6)	32·3 (5)	5·2 (5)
o-Cl	N(3) equatorial	0·0	48·9 (3)	0·0
	N(1) axial	44·2 (4)	35·3 (3)	4·1 (3)

The change in orientation can be attributed to the severe overcrowding that would arise for the Cl atom if the *o*-chlorophenyl compound adopted the orientation of the *p*-chlorophenyl compound. The substituent position also affects the axial aryl groups, since the orientation angle θ changes from 68·1 (6)° in the *p*-chlorophenyl compound to 44·2 (4)° in the *o*-chlorophenyl compound, in accord with the results for the *o*- and *p*-fluorophenyl compounds.

The N atoms are distinctly pyramidal in character, the N—C(aryl) bonds being inclined to the CH_2—N—CH_2 planes at 32·3 (5)–48·9 (3)° (Table 3). The out-of-plane angle in a tetrahedral arrangement of bonds is 54·7° and out-of-plane angles of 32·3 (5)–35·3 (3)° indicate that the N—C(axial) bonds in the *o*- and *p*-chlorophenyl compounds are bent outwards by 19–22° from the positions in an ideal chair conformer, alleviating the repulsion between the axial aryl groups. The largest out-of-plane angle, 48·9 (3)°, is for the equatorial aryl group at N(3) in the *o*-chlorophenyl compound, with zero lone-pair/π-orbital overlap. The N—C(aryl) bond here is 1·433 (4) Å, a little longer than the other N—C(aryl) bonds of 1·405 (8)–1·415 (3) Å in these molecules. The molecular geometry of aniline has been derived by *ab initio* gradient MO methods and the N—C bond length estimated to increase from 1·415 to 1·449 Å as the dihedral angle between the lone-pair orbital of the pyramidal N atom and the aromatic π orbitals changes from 0 to 90° (Niu & Boggs, 1984).

Atom N(3) of the *o*-chlorophenyl compound lies in the plane of the equatorial aryl group, whereas the other N atoms of the *o*- and *p*-chlorophenyl compounds deviate from their aryl planes by 0·101 (2)–0·158 (5) Å, corresponding to out-of-plane angles of 4·1 (3)–6·5 (5)° for the C(aryl)—N bonds. The MO calculations for aniline (Niu & Boggs, 1984) found that the C—N bond lies in the aromatic plane when the dihedral angle between the N lone-pair orbital and the aromatic π orbitals is 90° and that the out-of-plane angle for the C—N bond increases to 2·4° when the dihedral angle between the orbitals is 0°. The maximum out-of-plane angle for the C(aryl)—N bonds in the *o*- and *p*-chlorophenyl compounds is at N(3) in the *p*-chlorophenyl compound, where the N lone-pair/π-orbital dihedral angle is 0°, in qualitative agreement with the MO calculations.

The CH_2—N—CH_2 angles in the triazacyclohexane rings are 109·3–110·8 (2)° (*o*-Cl compound) and 108·7–110·6 (5)° (*p*-Cl compound), and the N—CH_2—N angles are 112·0–113·4 (3)° (*o*-Cl compound) and 110·5—112·0 (6)° (*p*-Cl compound). There are similar small differences in the *o*-, *m*- and *p*-fluorophenyl compounds where the CH_2—N—CH_2 angles are 108·2–110·7° and the N—CH_2—N angles are 110·5–113·0°. The torsion angles around the C—N bonds in the triazacyclohexane rings are 55·0–56·7 (2)° (*o*-Cl compound) and 55·6–58·9 (5)° (*p*-Cl compound).

In solution, facile conformational interconversion in both compounds results in averaging of the ^1H NMR signals of the axial and equatorial CH_2 H atoms, which appear as a narrow singlet at *ca* δ 4·7 ($CDCl_3$).

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Acta Cryst. (1990). C**46**, 414–417

Structures of (Methyl)phenylhydrazone Derivatives and their Nonlinear Optical Properties

BY ERIKO CHIBA, KATSUHIKO TANI AND MIWA SHUTO

Research and Development Center, Ricoh Company Ltd, 16-1 Shin'ei-cho, Kohoku-ku, Yokohama, Kanagawa 223, Japan

AND NOBUHIKO HAGA AND MASAYASU TOKONAMI

Faculty of Science, The University of Tokyo, 3-1 Hongo 7-chome, Bunkyo-ku, Tokyo 113, Japan

(*Received 29 November 1988; accepted 1 June 1989*)

Abstract. The crystal structures of two (methyl)-phenylhydrazone derivatives, which showed very different second-harmonic generation (SHG) efficiencies, were determined by X-ray diffraction at room temperature with Mo $K\alpha$ radiation (λ = 0·7107 Å). 3-Methylbenzaldehyde *N*-methyl-*N*-phenylhydrazone (Me-BMPH): $C_{15}H_{16}N_2$, M_r = 224·3, monoclinic, $P2_1/a$, a = 12·106 (3), b = 18·398 (8), c = 5·800 (2) Å, β = 91·92 (2)°, V = 1291·1 (7) Å^3, Z = 4, D_x = 1·154, D_m = 1·160 g cm^{-3} (293 K), μ = 0·64 cm^{-1}, $F(000)$ = 480; the final R was 0·056 for 1421 significant observed reflections. 3-Methoxybenzaldehyde *N*-methyl-*N*-phenylhydrazone (MeO-BMPH): $C_{15}H_{16}N_2O$, M_r = 240·3, monoclinic, $P2_1$, a = 13·975 (2), b = 7·953 (1), c = 5·933 (1) Å, β = 96·81 (1)°, V = 654·8 (2) Å^3, Z = 2, D_x = 1·219, D_m = 1·221 g cm^{-3} (293 K), μ = 0·73 cm^{-1}, $F(000)$ = 256; the final R was 0·053 for 748 significant observed reflections. The SHG efficiency, measured on a powder sample, is nearly zero for Me-BMPH, whereas it is 12·5 times that of urea standard for MeO-BMPH. Both molecules are nearly

0108-2701/90/030414-04$03.00