$$C_{21}H_{27}ClNO^+.C_4H_3O_4^-$$

species to the anionic fumarate. The hydrogen bond extends from the H atom bonded to the N atom to O2 of the fumarate species. The N—H···O bond angle is 175·8°, and the H(N)···O2 bond length is 1·76 Å, while the total separation between N and O2 is 2·70 Å. Besides this hydrogen bond, there are no intermolecular forces which can be singled out for mention. Finally, there are no detectable unusual van der Waals distances in the crystal.

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Structures of 2-Chloro-4-cyclohexylamino-6-methoxy-1,3,5-triazine and 2-Chloro-4-methoxy-6-piperidino-1,3,5-triazine

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Abstract. $C_{10}H_{15}ClN_4O$, triclinic, $P\bar{1}$, $M_r = 242.7$, $a = 6.817$ (1), $b = 7.967$ (1), $c = 12.018$ (1) Å, $\alpha = 85.01$ (1), $\beta = 73.80$ (1), $\gamma = 69.65$ (1)°, $V = 587.6$ Å^3, $Z = 2$, $D_x = 1.372$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1.54178$ Å, $\mu = 2.8$ mm^{-1}, $F(000) = 256$, $T = 295$ K, $R = 0.056$ for 1416 observed reflections. $C_9H_{13}ClN_4O$, monoclinic, $P2_1/n$, $M_r = 228.7$, $a = 6.571$ (1), $b = 13.090$ (1), $c = 12.855$ (2) Å, $\beta = 95.07$ (2)°, $V = 1101.4$ Å^3, $Z = 4$, $D_x = 1.379$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1.54178$ Å, $\mu = 3.0$ mm^{-1}, $F(000) = 480$, $T = 295$ K, $R = 0.076$ for 1299 observed reflections. The molecules of the two compounds show similar types of stacking, with triazine ring separations of 3·84 and 3·28 Å, respectively. The study shows the dependence of ring geometry not only upon the types and positions of substituents but also upon the Cl—C(ring) bond length.

Introduction. Although triazine molecules form a flat benzene-like aromatic system, their properties differ considerably from those of benzene due to the different atomic types in the ring. The most common triazines are 1,3,5-triazines (*s*-triazines), which are produced commercially from 2,4,6-trichloro-1,3,5-triazine. This compound easily exchanges its Cl atoms and is therefore a very reactive chlorination agent. The partial substitution of Cl atoms by alkoxy group(s) changes the course of reaction and, for example, 2-chloro-4,6-dialkoxy-1,3,5-triazines and carboxylic acids give reactive 2-alkanoyloxy intermediates, which under further treatment with alcohols or amines yield appropriate esters or amides (Kamiński, 1985, 1987).

To date we know of only two reports of crystal structures containing Cl—triazine bonds: 2-chloro-4-dimethylamino-6-triphenylphosphoranylidene-amino-1,3,5-triazine (Cameron, Mannan, Biddlestone & Shaw, 1975) and 2-(N'-acetylhydra-zino)-4,6-dichloro-1,3,5-triazine (Reck & Jankowsky, 1981). These reports, together with the structures reported here, provide an opportunity for studying the influence of chlorine substitution on the *s*-triazine ring.

Experimental. Prismatic crystals of 2-chloro-4-cyclohexylamino-6-methoxy-1,3,5-triazine (CCMT) and 2-chloro-4-methoxy-6-piperidino-1,3,5-triazine (CMPT) were obtained from methanol solutions by slow evaporation of the solvent. Crystals of dimensions 0·17 × 0·16 × 0·11 (CCMT) and 0·33 × 0·26 × 0·21 mm (CMPT) were used for data collection and unit-cell determination. Diffraction data were collected on a CAD-4 diffractometer with Cu $K\alpha$ radiation up to $\theta = 75$ and 65° for CCMT and CMPT, respectively. The unit-cell parameters were calculated from 25 reflections in the θ range 16–32° (CCMT)

and 20–28° (CMPT). The intensities of 2317 (2263 for CMPT) reflections were collected in the $\omega/2\theta$ scan mode. Ranges of h,k,l were 0–8, -9–9, -15–15 for CCMT and -8–8, 0–16, 0–16 for CMPT. Three standards showed 1 (CCMT) and 2% (CMPT) variation during data collection. The data were corrected for absorption according to Walker & Stuart (1983), maximum and minimum values of corrections being 1·38 and 1·29 for CCMT and 2·29 and 1·68 for CMPT.

The structures were solved by direct methods (Sheldrick, 1986) and refined with full-matrix least-squares methods on F (Sheldrick, 1976) to a final R = 0·056 and 0·076 (wR = 0·052 and 0·078; S = 0·945 and 0·971) based on 1416 and 1299 observed [$I \geq 3\sigma(I)$] reflections for CCMT and CMPT, respectively. Most H atoms were found from difference Fourier maps and all (except for the amine H atom in CCMT which was left free) were refined in the riding model due to poor quality of the crystals and resulting unsatisfactory number of observed reflections. The weighting scheme used was $w^{-1} = \sigma^2(F) + kF^2$, where $k = 0$ for CCMT and 0·003 for CMPT. The final cycle had 185 (CMPT 168) variables including anisotropic U_{ij} for non-H atoms and U_{iso} for H atoms, $(\Delta/\sigma)_{max}$ = 0·03 and an isotropic extinction parameter (Larson, 1967) g = 0·009 (2) and 0·002 (1) (CMPT). The $\rho_{max}(\rho_{min})$ on the final ΔF maps were 0·15 ($-0·16$) and 0·19 ($-0·21$) e Å^{-3} for CCMT and CMPT, respectively. Atomic scattering factors for neutral atoms were those included in *SHELX76* (Sheldrick, 1976). The calculations were performed on an Amstrad PC 1512 microcomputer.

The final atomic coordinates are given in Table 1.*

Discussion. The atomic numbering schemes and views of the CCMT and CMPT molecules are shown in Fig. 1, while selected bond lengths, valency and torsional angles are listed in Table 2.

The s-triazine rings in CCMT and CMPT show the characteristic angular pattern (N—C—N angles > 120° and C—N—C < 120°) observed in all s-triazine derivatives. A strong repulsion between σ electrons of each N—C bond and the lone-pair electrons of the N atom would explain the decrease in the C—N—C ring angles, while an increase in ring N—C—N angles results from the attraction of σ C—X electrons towards the substituent atom X, thus reducing the repulsion between these electrons and those of the ring C—N bonds (Cameron, Mannan, Biddlestone & Shaw, 1975; Domenicano, Vaciago &

* H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53373 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters for non-H atoms*

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{eq}(\text{Å}^2)$
CCMT				
Cl(1)	0·0102 (3)	0·3181 (2)	0·7139 (1)	5·28 (7)
N(1)	$-0·0760$ (8)	0·2518 (5)	0·9347 (3)	3·16 (16)
C(2)	$-0·1039$ (10)	0·3792 (7)	0·8585 (4)	3·26 (18)
N(3)	$-0·2107$ (8)	0·5537 (6)	0·8750 (3)	3·40 (15)
C(4)	$-0·2917$ (9)	0·5953 (6)	0·9880 (4)	3·00 (18)
O(4)	$-0·4045$ (7)	0·7716 (4)	1·0081 (3)	3·94 (13)
N(5)	$-0·2774$ (7)	0·4874 (5)	1·0759 (3)	2·95 (15)
C(6)	$-0·1643$ (9)	0·3124 (6)	1·0460 (4)	2·85 (17)
N(7)	$-0·1379$ (8)	0·1945 (5)	1·1298 (3)	3·41 (16)
C(8)	$-0·2222$ (10)	0·2469 (6)	1·2540 (4)	3·17 (18)
C(9)	$-0·0502$ (10)	0·1673 (7)	1·3175 (4)	3·49 (19)
C(10)	$-0·1395$ (12)	0·2334 (8)	1·4444 (4)	4·29 (24)
C(11)	$-0·3493$ (13)	0·1958 (9)	1·5028 (4)	4·88 (24)
C(12)	$-0·5155$ (11)	0·2678 (9)	1·4359 (5)	4·82 (26)
C(13)	$-0·4258$ (11)	0·1995 (8)	1·3094 (5)	4·14 (21)
C(40)	$-0·4896$ (12)	0·8330 (7)	1·1265 (5)	4·52 (24)
CMPT				
Cl(1)	0·2331 (3)	0·2474 (1)	0·4027 (1)	4·60 (5)
N(1)	0·2636 (7)	0·1165 (4)	0·5529 (3)	2·44 (13)
C(2)	0·2429 (9)	0·1225 (5)	0·4498 (4)	2·77 (16)
N(3)	0·2267 (8)	0·0516 (4)	0·3786 (3)	2·89 (13)
C(4)	0·2325 (9)	$-0·0422$ (5)	0·4221 (4)	2·60 (16)
O(4)	0·2163 (7)	$-0·1171$ (4)	0·3528 (3)	3·52 (12)
N(5)	0·2530 (7)	$-0·0646$ (3)	0·5225 (3)	2·37 (12)
C(6)	0·2709 (8)	0·0180 (4)	0·5866 (4)	2·03 (15)
N(7)	0·2943 (8)	0·0009 (4)	0·6905 (3)	2·65 (12)
C(8)	0·3355 (13)	0·0828 (5)	0·7650 (5)	3·66 (17)
C(9)	0·2049 (15)	0·0718 (6)	0·8557 (6)	4·83 (25)
C(10)	0·2324 (15)	$-0·0337$ (6)	0·9050 (5)	4·58 (24)
C(11)	0·1857 (11)	$-0·1156$ (6)	0·8227 (5)	3·94 (20)
C(12)	0·3146 (11)	$-0·1018$ (5)	0·7330 (5)	3·46 (21)
C(40)	0·2242 (13)	$-0·2199$ (5)	0·3924 (5)	4·21 (21)

Table 2. *Selected bond lengths (Å) and angles (°) for CCMT and CMPT*

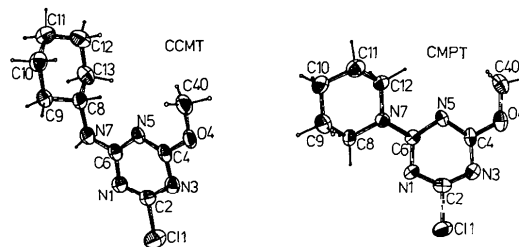|	CCMT	CMPT
N(1)—C(2)*	1·307 (6)	1·322 (7)
N(1)—C(6)	1·358 (5)	1·360 (7)
N(3)—C(2)	1·329 (6)	1·302 (8)
N(3)—C(4)	1·338 (5)	1·348 (8)
N(5)—C(4)	1·306 (5)	1·320 (7)
N(5)—C(6)	1·359 (5)	1·358 (7)
C(2)—Cl	1·729 (4)	1·742 (6)
C(4)—O	1·352 (5)	1·322 (7)
C(6)—N(7)	1·317 (6)	1·349 (7)
Cl—C(2)—N(1)	117·2 (4)	113·7 (5)
Cl—C(2)—N(3)	113·4 (3)	115·3 (4)
N(1)—C(2)—N(3)	129·4 (4)	131·0 (6)
N(3)—C(4)—N(5)	128·0 (4)	127·2 (5)
N(5)—C(6)—N(1)	124·0 (4)	124·2 (5)
C(2)—N(3)—C(4)	111·2 (4)	111·2 (5)
C(4)—N(5)—C(6)	114·2 (4)	114·4 (5)
C(6)—N(1)—C(2)	113·1 (4)	112·0 (5)

* Numbering of atoms refers to that of CCMT.

Fig. 1. Overall views and atomic labeling schemes for CCMT (left) and CMPT (right) (Johnson, 1976).
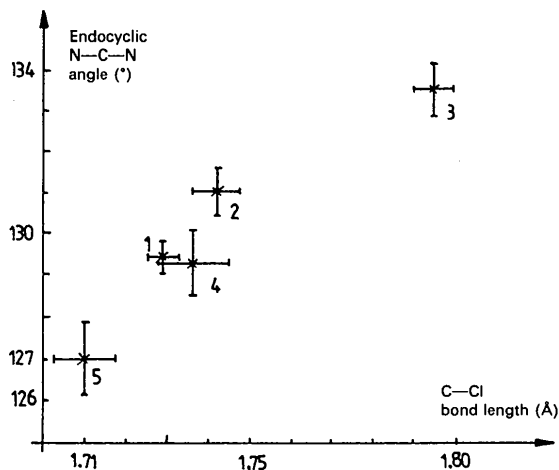
Fig. 2. Relationships between Cl–triazine bond length and endocyclic N—C—N angle. The points shown refer to: 1 CCMT; 2 CMPT; 3 2-chloro-4-dimethylamino-6-triphenylphosphoranylideneamino-1,3,5-triazine (Cameron, Mannan, Biddlestone & Shaw, 1975); 4 and 5 2-(N′-acetylhydrazino)-4,6-dichloro-1,3,5-triazine (Reck & Jankowsky, 1981). Bars represent e.s.d.'s.

Coulson, 1975). The sensitivity of N—C—N ring angles in chloro-*s*-triazines to electronic effects is revealed in Fig. 2 which suggests that the N—C—N angle is positively correlated with the length of the bond from the central C atom to its chlorine substituent.

The average C—Cl bond distance in *s*-triazines and benzene derivatives is the same (about 1·74 Å) but the reactivity of chloro-*s*-triazines exceeds manyfold that of chlorobenzene due to substitution of

C(sp^2) by more electronegative N(sp^2) atoms at *ortho* and *para* positions in the *s*-triazine ring.

The *s*-triazine rings of the two chlorotriazine derivatives show partial stacking in the solid: the distances between the rings are 3·84 and 3·28 Å for CCMT and CMPT, respectively. Due to the conjugation between lone-pair electrons at the N atom of the piperidine moiety and the *s*-triazine system in CMPT, flattening of the piperidine ring at the N atom is observed and the sum of the three C—N(7)—C angles is 359·1° (Table 2).

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Structure of the 4-Oxo-2-butenoic Acid Alkyl Ester Moiety. II. Structure of Dimethyl 4,4′-(Methylhydrazo)bis(4-oxo-2-butenoate)

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Abstract. Dimethyl *N*-methyl-4,4′-dioxo-4,4′-hydrazo-2-butenoate, $C_{11}H_{14}N_2O_6$, $M_r = 270·24$, triclinic, $P\bar{1}$, $a = 4·604$ (1), $b = 8·543$ (1), $c = 16·940$ (1) Å, $\alpha = 85·60$ (1), $\beta = 89·21$ (1), $\gamma = 85·97$ (1)°, $V = 662·7$ Å^3, $Z = 2$, $D_x = 1·354$ Mg m^{-3}, $\lambda(Cu\ K\alpha) = 1·54178$ Å, $\mu = 0·91$ mm^{-1}, $F(000) = 284$, $R = 0·060$ for 2276 reflections. The molecules in the crystal form chains by means of N—H⋯O hydrogen bonds [N⋯O distance 2·794 (2) Å] running in the [100] direction. The configurations at the C=C