Table 4. *Comparison of some geometrical parameters for non-substituted and chloro-substituted compounds (e.s.d.'s are about* 0.002 Å *for distances and* 0.2° *for angles*)

		n_Nd_N (Å)	N···π (Å)	*X*	*X*···π (Å)	N···*X* (Å)	N—C—C—*X* (°)
Phenyl side				>N—			
This work	4	7.10	0.09		0.08	2.90	55.7
(*B*I)*	4	7.08	−0.25		0.12	2.89	−57.7
Pyrrolidine side				OH			
This work		6.42†	1.13		2.40	3.74	−171.7
(*B*I)*		6.17	0.31		−2.19	3.72	173.7

* Stadnicka, Ciechanowicz-Rutkowska & Malawska (1991).
† Distance of N atom from the midpoint between C(4) and C(3).

drugs interact with the receptor their molecules can be treated neither as free nor as restrained by exactly the same force field as in the crystal lattice. NMR studies are planned to determine the conformer population in solution.

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Structure of 1,3,5-Tribenzoylperhydro-1,3,5-triazine

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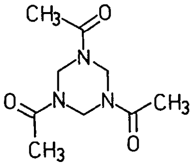
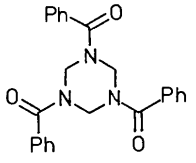
Abstract. $C_{24}H_{21}N_3O_3$, $M_r = 399.45$, orthorhombic, $Pna2_1$, $a = 11.313$ (1), $b = 19.187$ (1), $c = 9.6363$ (9) Å, $V = 2091.6$ (3) Å^3, $Z = 4$, $D_x = 1.268$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.08$ mm^{-1}, $F(000) = 840$, $T = 298$ K, $R = 0.060$ for 1605 unique reflections. The molecular structure is asymmetric and the N atoms have approximate trigonal structures. The crystals show significant second-order harmonic generation and a short cut-off wavelength for absorption (298 nm).

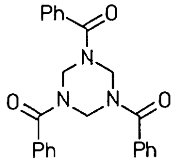
Introduction. While the molecular structures and intramolecular motions of 1,3,5-trialkyl- (or triaryl-) perhydro-1,3,5-triazines in the crystalline state as well as in the liquid phase have been extensively studied (Sim, 1987; Zangrando, Poggi, Giumanini & Verardo, 1987; Bouchemma, McCabe & Sim, 1988, 1990), those of 1,3,5-triacyl- (or triaroyl-) perhydro-1,3,5-triazines are much less well known. The crystal structure data of the latter have been found only for 1,3,5-triacetylperhydro-1,3,5-triazine (1) (Choi, Santoro & Marinkas, 1975) in the Cambridge Structural Database (1991).



(1)



(2*a*)



(2*b*)

Katritzky and his coworkers revealed that the title compound (2) exists as a mixture of the C_3 symme-

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tric conformer (2*a*) and the asymmetric conformer (2*b*) with the population ratio of 36.5:63.5 in the liquid phase (Katritzky, Murugan, Luce, Chen, Brey & Zerner, 1987). We report here the structure of (2) determined by X-ray crystallographic analysis and its potential as a new second-order optical material.

Experimental. The title compound (2) was prepared by the literature method (Tracy, 1976) and was recrystallized from ethanol, m.p. 512.5–515.0 K, crystal size 0.50 × 0.45 × 0.25 mm. D_m not determined. A Rigaku AFC5 diffractometer equipped with a graphite monochromator was used to collect the data. The cell dimensions were obtained from the least-squares refinement of 50 θ values in the range $20 < 2\theta < 30°$. The data were collected using the θ–2θ scan technique at a θ rate of 4.0° min^{-1} with a 2θ range 3.0–60.0°. Data having $0 \le h \le 14$, $0 \le k \le 26$, $0 \le l \le 13$ were measured. Three reflections (200, 040, 002) were measured every 150 reflections to monitor instrument and crystal stability, intensity variation ≤ 1.7%. The number of reflections measured was 2795. 1671 reflections with $I > \sigma(I)$ were considered observed, 1605 were unique. The data were corrected for Lp effects, but not for absorption.

The structure was solved by direct methods and refined by the full-matrix least-squares method. The number of the parameters refined was 291. The non-H atoms were refined with anisotropic temperature factors. All of the H atoms were calculated in idealized positions and their isotropic temperature factors were refined by fixing the coordinates. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/[\sigma^2(F) + 0.0002F^2]$. In the final least-squares refinement, $R = 0.060$, $wR = 0.051$, $S = 1.634$ and $(\Delta/\sigma)_{\max} = 0.197$. The maximum and the minimum heights in the final difference Fourier synthesis were 0.36 and −0.48 e Å^{-3}, respectively. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All the crystallographic calculations were performed using *XTAL*3.0 (Hall & Stewart, 1990).

The UV spectra were measured on a JASCO Ubest-50 spectrometer.

Discussion. Atomic coordinates and selected geometrical parameters are given in Tables 1 and 2, respectively.[*] A perspective view of the molecule is given in Fig. 1. It shows that (2) exists exclusively as an asymmetric conformer which can be represented by the formula (2*b*). This is in sharp contrast to the structure of (1), which adopts the C_3 symmetric conformation as represented by (1).

Table 1. *Non-H-atom positional and isotropic displacement parameters* (Å^2), *with e.s.d.'s in parentheses*

$$U_{\rm eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	$U_{\rm eq}$
C(1)	−0.0700 (4)	0.6694 (2)	0.62377	0.057 (2)
C(2)	0.0377 (4)	0.5968 (2)	0.4604 (7)	0.055 (2)
C(3)	0.0470 (4)	0.7237 (2)	0.4417 (7)	0.064 (2)
C(4)	0.0446 (5)	0.7784 (2)	0.6704 (8)	0.068 (2)
C(5)	0.0532 (4)	0.5761 (2)	0.7141 (8)	0.057 (2)
C(6)	0.2268 (4)	0.6576 (2)	0.4039 (7)	0.063 (2)
C(7)	−0.0155 (4)	0.7882 (2)	0.8055 (8)	0.063 (2)
C(8)	0.0517 (7)	0.7906 (3)	0.926 (1)	0.095 (3)
C(9)	0.003 (1)	0.8045 (4)	1.050 (1)	0.131 (4)
C(10)	−0.114 (1)	0.8177 (4)	1.059 (1)	0.119 (4)
C(11)	−0.1840 (7)	0.8177 (3)	0.942 (1)	0.104 (3)
C(12)	−0.1348 (5)	0.8015 (2)	0.8132 (9)	0.077 (2)
C(13)	0.1112 (4)	0.5065 (2)	0.6963 (7)	0.058 (2)
C(14)	0.2097 (5)	0.4912 (3)	0.7769 (8)	0.080 (2)
C(15)	0.2597 (5)	0.4258 (3)	0.776 (1)	0.102 (3)
C(16)	0.2089 (6)	0.3741 (3)	0.695 (1)	0.099 (3)
C(17)	0.1134 (6)	0.3884 (3)	0.6126 (8)	0.079 (2)
C(18)	0.0645 (4)	0.4539 (2)	0.6133 (7)	0.062 (2)
C(19)	0.2866 (4)	0.5889 (2)	0.3814 (7)	0.058 (2)
C(20)	0.3846 (5)	0.5728 (3)	0.4602 (8)	0.089 (2)
C(21)	0.4456 (7)	0.5110 (4)	0.437 (1)	0.128 (4)
C(22)	0.4091 (9)	0.4679 (4)	0.333 (1)	0.134 (4)
C(23)	0.3141 (7)	0.4827 (3)	0.254 (1)	0.106 (3)
C(24)	0.2521 (5)	0.5440 (3)	0.2783 (8)	0.081 (2)
N(1)	0.0029 (3)	0.7286 (2)	0.5827 (6)	0.055 (1)
N(2)	−0.0040 (3)	0.6048 (2)	0.6022 (6)	0.049 (1)
N(3)	0.1078 (3)	0.6581 (2)	0.4214 (6)	0.053 (1)
O(1)	0.1254 (4)	0.8173 (2)	0.6355 (7)	0.113 (2)
O(2)	0.0518 (4)	0.6045 (2)	0.8273 (6)	0.086 (1)
O(3)	0.2840 (3)	0.7116 (2)	0.4028 (7)	0.099 (2)

The perhydro-1,3,5-triazine ring adopts a chair conformation with approximate C_3 symmetry. The C—N ring bond lengths [1.446 (6)–1.467 (6) Å] are in the range of those observed for (1) and 1,3,5-triarylperhydro-1,3,5-triazines (Choi, Santoro & Marinkas, 1975; Bouchemma, McCabe & Sim, 1990). The C—N—C and N—C—N ring bond angles show nearly the same values [the mean values are 113.4 (4), 109.7 (4)°, respectively]. The absolute values of the torsion angles of the ring are nearly the same [the mean value is 54.5 (5)°].

While atoms N(1) and N(3) are planar, atom N(2) is slightly pyramidal. Thus, the deviation of N(1) from the plane of C(1), C(3) and C(4) is 0.056 (6) Å, that of N(2) from the plane of C(1), C(2) and C(5) −0.145 (6) Å, and that of N(3) from the plane of C(2), C(3) and C(6) −0.085 (6) Å. The bond angle of the N atom with the N—C bond *anti* to the C=O bond is always significantly larger than that with the N—C bond *syn* to the C=O bond. Thus, the angle C(1)—N(1)—C(4) is larger than C(3)—N(1)—C(4), C(2)—N(2)—C(5) larger than C(1)—N(2)—C(5) and C(2)—N(3)—C(6) larger than C(3)—N(3)—C(6). A similar arrangement was observed for (1).

Each of the benzene rings is nearly perpendicular to the least-squares plane of the perhydro-1,3,5-triazine ring (plane 1). The angle of plane 1 and the benzene ring with C(4) is 86.3 (3)°, the angle of plane 1 and the benzene ring with C(13) 89.2 (2)°, and the

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[*] Lists of H-atom coordinates, anisotropic parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54813 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0533]

Table 2. *Selected geometrical parameters* (Å, °)

The e.s.d.'s for the parameters including H atoms are not given because the coordinates of the H atoms were fixed in the least-squares refinement as stated in *Experimental*.

N(1)—C(1)	1.457 (5)	N(2)—C(1)	1.462 (5)	N(3)—C(2)	1.467 (6)
N(1)—C(3)	1.450 (9)	N(2)—C(2)	1.454 (9)	N(3)—C(3)	1.446 (6)
N(1)—C(4)	1.361 (8)	N(2)—C(5)	1.373 (8)	N(3)—C(6)	1.357 (6)
C(4)—O(1)	1.227 (7)	C(5)—O(2)	1.220 (9)	C(6)—O(3)	1.221 (6)
C(4)—C(7)	1.48 (1)	C(5)—C(13)	1.497 (6)	C(6)—C(19)	1.496 (6)
C(1)—N(1)—C(3)	113.5 (3)	C(1)—N(2)—C(2)	112.9 (4)	C(2)—N(3)—C(3)	113.9 (4)
C(1)—N(1)—C(4)	125.1 (5)	C(2)—N(2)—C(5)	122.9 (4)	C(2)—N(3)—C(6)	124.2 (3)
C(3)—N(1)—C(4)	120.5 (4)	C(1)—N(2)—C(5)	118.0 (4)	C(3)—N(3)—C(6)	119.7 (3)
N(1)—C(1)—N(2)	109.5 (3)	N(2)—C(2)—N(3)	109.3 (4)	N(3)—C(3)—N(1)	110.3 (5)
N(1)—C(4)—O(1)	121.0 (7)	N(2)—C(5)—O(2)	121.1 (4)	N(3)—C(6)—O(3)	121.3 (4)
N(1)—C(4)—C(7)	118.5 (5)	N(2)—C(5)—C(13)	118.4 (6)	N(3)—C(6)—C(19)	118.3 (4)
O(1)—C(4)—C(7)	120.4 (6)	O(2)—C(5)—C(13)	120.5 (6)	O(3)—C(6)—C(19)	120.4 (4)
C(4)—C(7)—C(8)	119.2 (5)	C(5)—C(13)—C(14)	118.5 (5)	C(6)—C(19)—C(20)	118.8 (5)
C(3)—N(1)—C(1)—N(2)	55.0 (5)	N(1)—C(1)—N(2)—C(2)	−56.0 (4)	C(1)—N(2)—C(2)—N(3)	55.2 (5)
N(2)—C(2)—N(3)—C(3)	−54.0 (6)	C(2)—N(3)—C(3)—N(1)	53.2 (6)	N(3)—C(3)—N(1)—C(1)	−53.7 (5)
C(1)—N(1)—C(4)—C(7)	−20.7 (7)	C(2)—N(2)—C(5)—C(13)	−35.5 (6)	C(2)—N(3)—C(6)—C(19)	19 (1)
N(1)—C(4)—C(7)—C(12)	−55.6 (7)	N(2)—C(5)—C(13)—C(18)	−35.8 (8)	N(3)—C(6)—C(19)—C(24)	54.1 (9)
O(1)—C(4)—N(1)—C(3)	−4.7 (7)	O(2)—C(5)—N(2)—C(1)	−2.0 (7)	O(3)—C(6)—N(3)—C(3)	−1 (1)
C(4)—N(1)—C(3)—H(031)	−1	C(5)—N(2)—C(1)—H(011)	−25	C(6)—N(3)—C(3)—H(031)	12

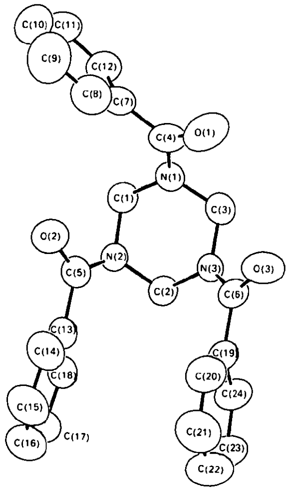

Fig. 1. Perspective view of the molecule.

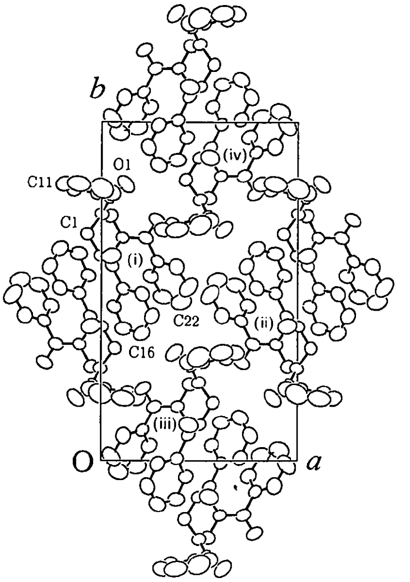

Fig. 2. Packing diagram viewed down the *c* axis. Symmetry operations: (i) *x*, *y*, *z*; (ii) −*x*, −*y*, 0.5 + *z*; (iii) 0.5 − *x*, 0.5 + *y*, 0.5 + *z*; (iv) 0.5 + *x*, 0.5 − *y*, *z*.

angle of plane 1 and the benzene ring with C(19) 87.4 (3)°. The angle of the benzene ring with C(13) and that with C(19) is 166.7 (3)°.

In each of the *N*-benzoyl groups, the dihedral angle between the N—C=O plane and the benzene ring substantially deviates from 0° [55.4 (5) for N(1), 144.7 (4) for N(2) and 127.1 (3)° for N(3)]. This is in accordance with the geometrical features frequently observed for aroyl amides. Among 62 absolute values of the dihedral angle between the N—C=O plane and the aromatic ring extracted from the Cambridge Structural Database files, 44 values are in the range 40–130°.

Of the intramolecular nonbonding atom pairs separated by four or more bonds, there are three pairs in which the separation is less than the sum of the relevant van der Waals radii (Bondi, 1964): O(1)···H(031) (2.37 Å), O(2)···H(011) (2.32 Å) and O(3)···H(031) (2.21 Å), where H(031) and H(011) are the equatorial H atoms on C(3) and C(1), respectively. These contacts are due to the approximate coplanarity of the sequence O=C—N—C—H, as shown by the small absolute values of the relevant torsion angles in the sequence. The fact that the absolute magnitude of torsion angle C(5)—N(2)—C(1)—H(011) is distinctly larger than that of C(4)—N(1)—C(3)—H(031) and of C(6)—N(3)—C(3)—H(031) is consistent with the slight pyramidality of N(2).

The crystal structure is shown in Fig. 2. Two molecules interrelated by C_2 symmetry form a dimerlike pair. There are no intermolecular distances significantly shorter than the sum of the relevant van der Waals radii.

The crystals of (2) showed a significant powder second-order harmonic generation for a fundamental wavelength of 1.064 μm but with poor reproducibility, the origin of which is under investigation. The UV spectrum of the isopropyl alcohol solution showed $\lambda_{\max} = 220$ nm ($\varepsilon = 21605$) and no absorption at λ longer than 298 nm. Such a short cut-off wavelength and a significant powder efficiency of (2) deviate substantially from the undesireable trade-off relationship between the two quantities commonly observed for second-order nonlinear organic materials (Itoh, Oono, Isogai & Kakuta, 1989). Further details of the optical properties of (2) will be reported elsewhere.

We thank Professor Sydney R. Hall of the University of Western Australia for many instructions for the use of *Xtal*3.0, and Drs Atsushi Kakuta and Yuzo Itoh of Hitachi Ltd for the measurement of the second-order harmonic generation and helpful discussions. We are grateful to the Japanese Ministry of Education, Science and Culture for the Grant-in-Aid 02640384.

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2,8-Dioxo-2,8-diphenoxy-1,3,7,9-tetraaza-2λ^5,8λ^5-diphosphatricyclo[7.3.0.0^{3,7}]dodekan

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Abstract. 2,8-Diphenoxy-1,3,7,9-tetraaza-2λ^5,8λ^5-diphosphatricyclo[7.3.0.0^{3,7}]dodecane 2,8-dioxide, $C_{18}H_{22}N_4O_4P_2$, $M_r = 420.346$, monoclinic, $P2_1/c$, $a = 6.995\,(2)$, $b = 14.902\,(5)$, $c = 9.803\,(4)$ Å, $\beta = 110.33\,(3)°$, $V = 958\,(1)$ Å^3, $Z = 2$, $D_x = 1.457$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.25$ mm^{-1}, $F(000) = 440$, $T = 293$ K, $R = 0.054$ ($wR = 0.028$) for 1836 unique contributing reflections. The compound was synthesized in our laboratory for a comparison of its ring conformation with those of other 1,2,4,5-tetraaza-3λ^5,6λ^5-phosphacyclohexanes. The saturated six-membered ring of the isolated *E* isomer adopts a chair conformation. The terminal O atoms at P are in equatorial positions, the phenoxy groups in axial positions. Bond distances: N—N 1.448 (3), P=O 1.454 (2), P—O 1.589 (2), P—N 1.671 (2) and 1.633 (3), N—C 1.472 (4) and 1.481 (3) Å.

Einleitung. Cyclische Dihydrazide vom Typ (1) besitzen in vielen Fällen eine Twist-Konformation. Dies hängt in großem Maße von der Raumbeanspruchung der Ringsubstituenten ab (Engelhardt & Stromburg, 1985; und die dort zitierte Literatur). *N*-Tetramethylierte Verbindungen liegen in den bisher untersuchten Fällen vom Typ (1*b*) stets in Twist-Konformation vor. Bei nicht *N*-methylierten Molekülen (1*a*) ist die Twist-Konformation nur dann begünstigt, wenn besonders sperrige Substituenten in 3,6-Stellung *cis* zueinander stehen. Der Effekt der Substituenten an den N-Atomen besteht in einer Aufweitung der Torsionswinkel um die N—N-Bindungen. Da diese Torsionswinkel in einer Twist-Konformation größer sind als in einer Sessel-Konformation, wird erstere durch Substituenten an den N-Atomen begünstigt. Sind die Substituenten dagegen Glieder eines annellierten Ringes, so ist der

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