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Crystal Engineering of Some 2,4,6-Triaryloxy-1,3,5-triazines: Octupolar Nonlinear Materials

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Abstract: The principles of crystal engineering have been used to design a family of structures with potential as octupolar nonlinear optical (NLO) materials. The major aim in such an exercise, a carry-over of molecular symmetry into the crystal, is possible with a retrosynthetic approach. An appropriate choice of precursor trigonal molecules leads from the concept of the dimeric Piedfort unit. The crystal structures and NLO properties of a series of 2,4,6-triaryloxy-1,3,5-triazines, **1**−**6**, are reported. These compounds consistently form quasi-trigonal or trigonal networks that are two-dimensionally noncentrosymmetric. Substitutional variations on the phenyl moieties that were expected to maintain or to perturb this trigonal network have been explored. Molecular nonlinearities have been measured by Harmonic Light Scattering (HLS) experiments. Among the compounds studied, 2,4,6-triphenoxy-1,3,5-triazine, **1** adopts a noncentrosymmetric crystal structure with a measurable SHG powder signal. All these crystal structures are stabilized by weak intermolecular interactions such as herringbone, $\pi\cdots\pi$, C−H···O, and C−H···N hydrogen bonding. These octupolar molecules are more isotropic than the classical *p*-nitroaniline based dipolar NLO molecules, and this is advantageous from the viewpoint of potential electrooptic applications.

Introduction

Crystal engineering aims at the design of crystal structures of molecular solids with specific attributes, be they topological features, chemical functions, or physical properties.[1,2] Distinct aims and goals within the subject of crystal engineering may now be discerned:[3] (1) strategic and methodological concerns; (2) aesthetically motivated supramolecular synthesis based on symmetry, topology, and network properties; (3) efforts directed toward functional materials of practical importance[4] (nonlinear optics (NLO), ferromagnetism, microporosity, electronics, solid-state reactivity). Crystal engineering targeted at solids exhibiting large optical nonlinearities has attracted much interest.[5] Varied goals, ranging from fundamental to application-oriented, have converged so that optically nonlinear molecular crystals have been engineered all the way from optimized molecular units to state-of-the-art low-threshold optical parametric oscillators.[6,7]

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These efforts have been generally based on the dipolar paradigm wherein electron donating and withdrawing substituent groups interact via conjugated π-electron reservoirs such as a phenyl ring (e.g., *p*-nitroaniline, pNA and analogues),[8] two phenyl rings (stilbene and azo-dye derivatives),[9] or more elongated carotenoid push−pull structures.[10,11]

In polar molecule-based crystal engineering of NLO materials, the main aim is to ensure that a noncentrosymmetric assembly of molecular dipoles is established. This is a prerequisite for quadratic NLO effects[5] such as second harmonic generation (SHG) and for the cascading of such effects for cubic molecular dephasing.[12] A useful hierarchic classification of molecular crystal classes with respect to their quadratic nonlinear efficiency was established in the early 1980s and has served as a guideline for NLO crystals engineered with polar quasi one-dimensional molecules with a single dominant molecular hyperpolarizability coefficient along the charge-transfer axis.[13] At the magic angle of 54.7°, the inclination of the molecule within the unit cell provides optimal tradeoff between birefringence phase-matching constraints and enhancement of the effective molecular coefficient, as exemplified by the well-known substance *N*-(4-nitrophenyl)-L-prolinol (NPP).[7,14] However, the significant ground-state dipole moment in pNA-like dipolar molecules has been recognized as being detrimental toward the establishment of a noncentrosymmetric structure because dipole−dipole interactions tend to favor antiparallel stacking of neighboring molecular units. Reducing the ground state dipole moment while preserving optical nonlinearity had been a long-sought goal leading eventually to the push−pull structure of 3-methyl-4-nitropyridine-1-oxide (POM).[15]

The high anisotropy in these optimized structures[13] (pNA, NPP, POM) does not provide polarization independence, and they are therefore not the best-suited for NLO-type applications. More symmetrical molecules organized in more isotropic yet noncentrosymmetric arrays are expected to alleviate such problems. The traditional design of NLO active materials has concentrated exclusively on dipolar molecules and has thus ignored a wealth of possibilities that could arise from two- and three-dimensional self-assembly. Diversified investigations of more isotropic molecules with attached octupolar and multipolar nonlinearities have been proposed.[16−18] For example, 2,4,6-triamino-1,3,5-trinitrobenzene (TATB) has attracted much attention as the trigonal analogue of pNA.[16a,b,19] While octupolar nonlinearity has been experimentally demonstrated in molecular systems,[16c,d] its demonstration in supramolecular, that is crystalline, systems has remained a challenge.[20]

A typical symmetry pattern that leads to crystalline octupolar nonlinearity is the trigonal network **A** constituted with trigonal molecules (Figure 1). This two-dimensional network is noncentrosymmetric and arises from specific attractive interactions between structural elements that are schematically represented by bold and dashed lines.[16a] The main task in the crystal engineering of such a structure lies therefore in identifying the complementary elements and eventually a molecule that contains these elements in appropriate locations. This is not trivial. The carry-over of molecular symmetry into crystal symmetry (or even pseudosymmetry) is not expected from Kitaigorodskii's theory of close-packing,[21] and a majority of trigonal molecules routinely adopt close-packed crystal structures of low symmetry. This is so because there is little reason to expect that the symmetry of the supramolecular web surrounding *any* molecule should conform to the internal symmetry of the molecule itself.[22] Thus, the key to successfully extending molecular symmetry into the crystal lies in identifying a design strategy whereby the patterns of supramolecular interactions possess the (high) symmetry of the molecule. Of course, it is also necessary to ensure that the noncentrosymmetry of the two-dimensional network shown in **A** extends to the third dimension in the crystal, that is to bulk noncentrosymmetry. However, this is not the primary aim of this paper which concentrates on two-

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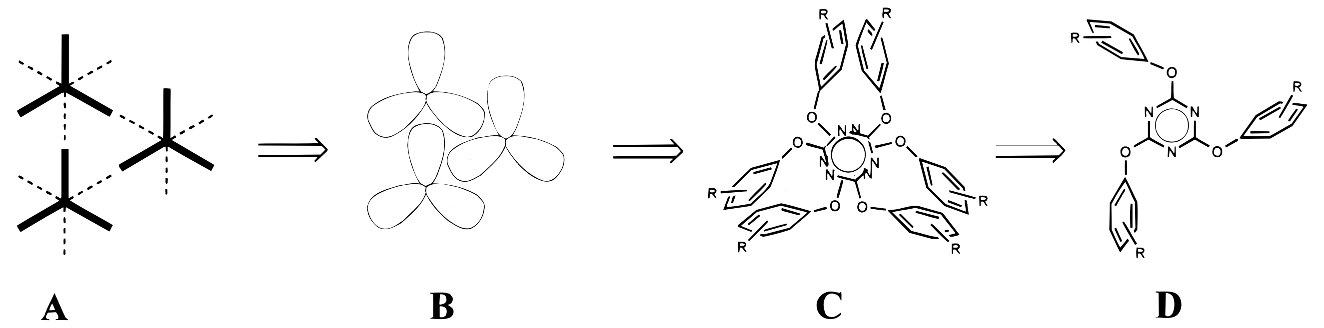

Figure 1. Retrosynthesis of a trigonal octupolar network. A. Trigonal network. B. Recognition of trigonal species. C. Stacked molecular diads of triazines. D. 2,4,6-Triaryloxy-1,3,5-triazine.

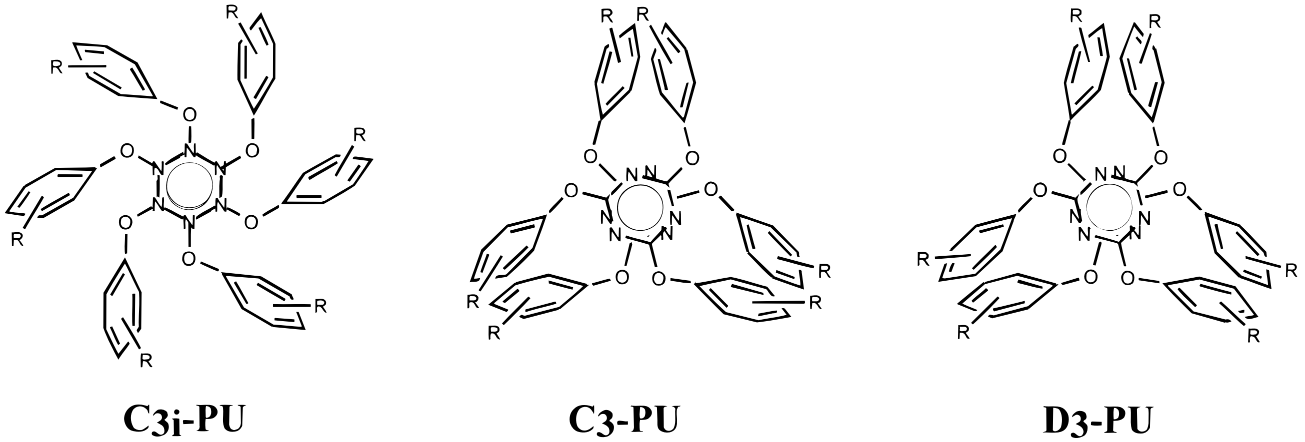

Figure 2. Piedfort units with 3-fold symmetry.

dimensional lamellar structures.[23] For a new family of potential octupolar NLO compounds, even this more limited goal of dissecting out critically large lower-dimensional noncentrosymmetric substructures is useful, and we show here that such trigonal networks are a common structural feature in the triazine family even when the overall crystal structures are centrosymmetric.[24]

Retrosynthetic analysis, as applied to network **A** (Figure 1), is not new to molecular synthesis, but its formal application to crystal engineering, that is supramolecular solid state synthesis, has been suggested only recently.[25] Considering a target crystal structure as a network, one may logically dissect it to identify structural units that are constructed with intermolecular interactions and ultimately arrive at the origin of the desired macroscopic architecture, that is the supramolecular synthons. These synthons are the crucial fusing elements of a crystal structure, and their identification can lead to molecular precursors that will yield the desired network structure upon crystallization. Accordingly, our search for a crystalline octupolar nonlinear material led us to think in terms of synthons such as **B**.

Crystalline triaryloxy substituted 1,3,5-triazines form stacked diads called Piedfort units (PUs).[26] PUs possessing C_{3i}, C_3, and D_3 symmetry (hereafter C_{3i}−PU, C_3−PU, and D_3−PU) have been identified[27] (Figure 2). Here we use the PU, which in itself is a supramolecular species **C**, as the starting point for the generation of higher level supramolecular assemblies. It was anticipated that synthon **C** of C_3 or D_3 symmetry PUs should lead to **B** en route to the desired trigonal network **A**. Such an ordered self-assembly was expected on the basis of specific electrostatic interactions between phenyl rings.[28] Retrosynthetic analysis of the PU **C** lead to substituted 2,4,6-triphenoxy-1,3,5-triazines **D** as starting materials for the generation of trigonal octupolar networks.[29] In summary, the retrosynthetic analysis **A** $\Rightarrow$ **B** $\Rightarrow$ **C** $\Rightarrow$ **D** had to take into account that the 3-fold molecular symmetry in **D** be faithfully transmitted at each level of the supramolecular hierarchy. Implied here is that at each level from **D** to **A**, only those combinations of intermolecular interactions that are consistent with high symmetry be optimized, while the numerous others that would be expected to lower the crystal symmetry be suppressed.

In this work we have investigated the crystal structures of the symmetrical 2,4,6-triaryloxy-1,3,5-triazines **1**−**6**, and have analyzed the effects of substitution on the network structures obtained. Halogen derivatives **7** and **8** are briefly mentioned. We discuss the reasons for the choice of the different molecular systems, the relationship among the observed crystal structures,

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[23] Suggestions for three-dimensional structural control have been proposed in refs 17b and 17c.

[24] Panunto, T. W.; Urbánczyk-Lipkowska, Z.; Johnson, R.; Etter, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 7786. These authors have demonstrated the merits of dissecting a structure, even of a centrosymmetric crystal, into constituent units which may be polar. These units have been termed “acentric”, and their identification may be useful in crystal engineering, provided they are large enough. The concept of local noncentrosymmetry is therefore a viable one in the intermediate stages of building up a (three-dimensionally) noncentrosymmetric crystal.

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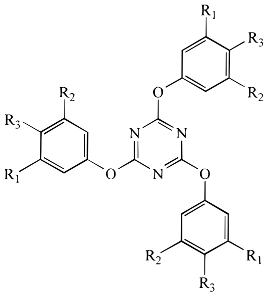
[29] The choice of triazines is also justified from the viewpoint of molecular engineering because the molecules have appreciable bond dipole moments. While the molecular 3-fold symmetry results in a net zero dipole moment, the magnitude of the individual dipoles ensures high octupole moments.

Table 1. Crystallographic Data for Triazines **1**−**6**

	1	**2**	**3**	**4**	**5**	**6**
emp. formula	$C_{21}H_{15}N_3O_3$	$C_{21}H_{12}N_3O_3Cl_3$	$C_{21}H_{12}N_3O_3Br_3$	$C_{24}H_{21}N_3O_3$	$C_{21}H_9N_3O_3Cl_6$	$C_{27}H_{27}N_3O_3$
formula wt.	357.36	460.69	594.07	399.44	564.01	441.52
crystal system	monoclinic	trigonal	trigonal	trigonal	trigonal	trigonal
space group	*Ia* (9)	*P*3*c*1 (165)	*P*3c1 (165)	*P*3c1 (165)	*P*3*c*1 (165)	*P*3*c*1 (165)
a (Å)	6.6010(13)	12.957(2)	13.1205(7)	13.023(2)	13.2925(6)	13.2987(13)
b (Å)	20.903(4)	12.957(2)	13.1205(7)	13.023(2)	13.2925(6)	13.2987(13)
c (Å)	12.649(3)	14.193(2)	14.4265(9)	14.334(3)	15.9132(9)	15.962(2)
α (deg)	90	90	90	90	90	90
β (deg)	97.93(3)	90	90	90	90	90
γ (deg)	90	120	120	120	120	120
Z	4	4	4	4	4	4
V (Å^3)	1728.6(6)	2063.6(5)	2150.8(2)	2105.3(6)	2435.0(2)	2444.8(4)
D_{calc} (Mg/m^3)	1.373	1.483	1.835	1.260	1.538	1.200
R_1	0.0832	0.0692	0.0448	0.0748	0.0956	0.0507
wR_2	0.2033	0.1546	0.1034	0.1624	0.2738	0.1320
GOF	1.126	1.156	1.070	0.996	1.111	1.009
N-total[a]	3685	2226	2330	2263	9070	2437
N-independent[b]	2044	902	947	920	1452	1072
variables	244	96	96	96	104	106
crystal shape[c]	needle	*h*-rod	*h*-rod	*h*-needle	*h*-tablet	*h*-rod
solvent	$CHCl_3$	$CHCl_3$	CH_2Cl_2	$CH_3CO_2C_2H_5$	$CHCl_3$	$CH_3CO_2C_2H_5$
C_k* [d]	0.69	0.66	0.66	0.65	0.63	0.64

[a] *N*-total is the total number of reflections collected. [b] *N*-independent is the number of independent reflections. [c] *h*-rod, *h*-needle, and *h*-tablet stand for hexagonal rod, hexagonal needle, and hexagonal tablet. [d] C_k* is the packing fraction calculated from the program PLATON.[34]



1 $R_1 = R_2 = R_3 = H$
2 $R_1 = Cl, R_2 = R_3 = H$
3 $R_1 = Br, R_2 = R_3 = H$
4 $R_1 = CH_3, R_2 = R_3 = H$
5 $R_1 = R_2 = Cl, R_3 = H$
6 $R_1 = R_2 = CH_3, R_3 = H$
7 $R_1 = R_2 = H, R_3 = Cl$
8 $R_1 = R_2 = H, R_3 = Br$

and our observations on molecular and crystal nonlinearities in this class of compounds.

Experimental Section

General Methods. Commercially available cyanuric chloride and the appropriate phenols were used as received without further purification. Reagent grade solvents were used for extraction, and distilled solvents were used for all recrystallizations.

General Procedure for the Synthesis of 2,4,6-Triaryloxy-1,3,5-triazines.[30] Cyanuric chloride (10 mmol) was heated with a small excess of the appropriate phenol (35 mmol) at 185−210° C for 5 h under a reflux air condenser. HCl gas was evolved vigorously during the first few hours. The crude reaction product was extracted with boiling EtOH leaving a residue of crude triaryloxytriazine. This residue was then recrystallized from $CHCl_3$ to give the pure crystalline product in 80−90% yield. All the triazines were characterized by their IR and NMR spectra.

X-ray Crystallography. Single crystals suitable for X-ray diffraction were grown from common organic solvents (Table 1). Data for **1** were collected on an Enraf-Nonius FAST area detector diffractometer and for **2**−**4** and **6** on a Siemens P4 diffractometer, while those for **5** were collected on a SMART diffractometer using Mo-*K*α radiation. The structure solutions and refinements were carried out using the programs SHELXS-86[31a] and SHELXL-93[31b] built-in with the Siemens SHELXTL (Version 5.03) package. The details of the X-ray data collection, structure solution, and refinement are given in the Supporting Information.

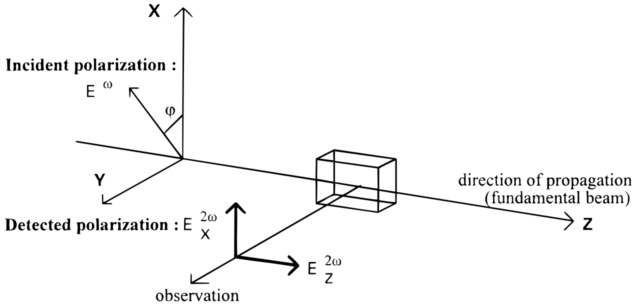


Figure 3. Laboratory reference frame (X,Y,Z) for the Harmonic Light Scattering (HLS) depolarization ratio measurements. The fundamental incoming beam propagates along Z and is polarized in the (X,Y) plane. The observation direction is along Y with the polarization analysis along X or Z.

NLO Measurements. The lack of a permanent dipole moment in the molecules studied here makes the classical Electric Field Induced SHG (EFISH) experiment unsuited to the determination of molecular nonlinearities, β.[32] We therefore performed measurements in solution by use of the HLS experiment.[16c,d,33] This incoherent nonlinear process results from the effect of room temperature fluctuations in centrosymmetric media on the optically nonlinear response and allows for the determination of the required orientational average $\langle\beta\otimes\beta\rangle$ of the β quadratic hyperpolarizability tensor. The $\langle\beta^2\rangle$ term of interest here has the additional advantage, with respect to EFISH, of being polarization dependent and thus reflects the tensorial nature of the molecular hyperpolarizability.

In the experimental setup (Figure 3), the fundamental pulsed Nd^{3+}:YAG near-IR source at 1.064 μm corresponds to a scattered second harmonic wavelength in the transparent region of the molecules of interest. Notably, all the compounds in this study are completely transparent in the visible region. The scattered intensity, collected at 90° from the incoming beam main axis, can be expressed as $I^{2\omega} = G(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle)(I^{\omega})^2$ for a solution with N_2 (respectively N_1) molecules per cm^3 of solute (respectively solvent; $CHCl_3$ in the present case), where the *G* coefficient includes geometrical factors and

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[30] Schaefer, F. C.; Thurston, J. T.; Dudley, J. R. *J. Am. Chem. Soc.* **1951**, *73*, 2990.

[31] (a) Sheldrick, G. M. SHELXS-86: Program for the Solution of Crystal Structures; University of Göttingen: Germany, 1986. (b) Sheldrick, G. M. SHELXL-93: An Integrated System for Refining and Displaying Crystal Structures from Diffraction Data; University of Göttingen: Germany, 1993.

[32] Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

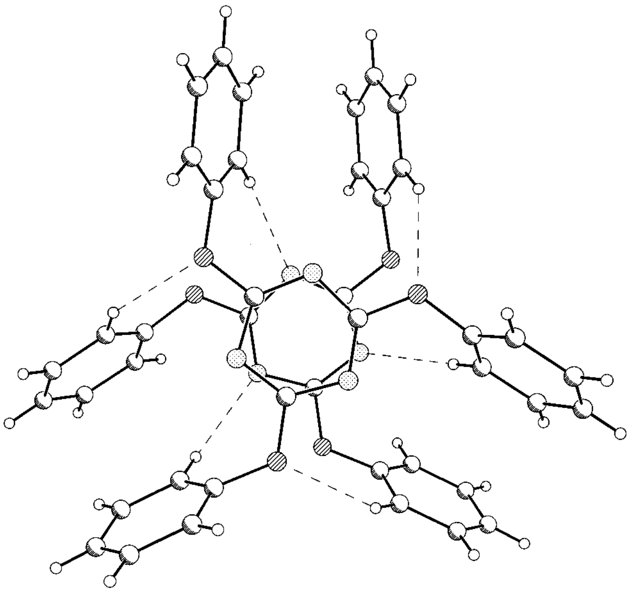

Figure 4. View down [100] showing a D_3−PU in **1**. C−H···O and C−H···N bonds are shown as dashed lines. Molecules related by *a*-glide form D_3−PUs.

experimental correction terms and where I^{ω} is the fundamental incident intensity. Further insight on molecular symmetry is available from polarized configurations of the HLS experiment.[17g] The overall $\langle\beta^2\rangle$ coefficient has two independent components, namely $\langle\beta^2{}_{XXX}\rangle$ (respectively $\langle\beta^2{}_{ZXX}\rangle$) measured for an analyzer parallel (respectively perpendicular) to the fundamental incident polarization. In this context, the evaluation of the depolarization ratio[17g] $D = \langle\beta^2{}_{ZXX}\rangle/\langle\beta^2{}_{XXX}\rangle$ helps determine the dipolar, octupolar, or mixed character of the nonlinear hyperpolarizability. This terminology arises from irreducible representation of the β tensor in a general spherical formalism. It has been shown[18] that the octupolar symmetry corresponds to a minimum of the depolarization ratio $D = 2/3$.

Results and Discussion

Table 1 gives the details of the crystallographic information for **1**−**6**. While crystals of triazine **1** are monoclinic, triazines **2**−**6** adopt trigonal space groups. It is of note that triazines **1**−**6** contain the trigonal network **A** in their crystal structures. Triazines **7** and **8** belong to the hexagonal crystal system and possess large cavities in their structures. The packing fractions[34] for triazines **1**−**6** (C_k*, Table 1) are in the range 0.63−0.69, typical of many close-packed organic solids. The description and analysis of the individual crystal structures is now presented.

Triazine 1 Crystallizes as a Unique Noncentrosymmetric Structure. Triazine **1** crystallizes in the noncentrosymmetric space group *Ia* (number 9).[35] D_3-symmetric Piedfort units (D_3−PUs) formed by an assembly of two molecules of **1** may be identified (Figure 4). The two molecules in the D_3−PU are related by an *a*-glide and are held together by $\pi\cdots\pi$ stacking interactions between triazine rings and also by C−H···O and C−H···N hydrogen bonds.[36] One of the molecule in the D_3−PU donates three C−H···O hydrogen bonds to the other which in turn donates three C−H···N hydrogen bonds back to the first. The molecules of **1** use *ortho* H-atoms of the phenoxy groups for such hydrogen bonding. In effect, a D_3−PU is stabilized by $\pi\cdots\pi$ interactions and six weak (C−H···O and C−H···N) hydrogen bonds. The geometrical parameters for these interactions are given in Table 2.

Table 2. Geometrical Parameters for Various Interactions in the Structure of **1**

interaction[a]	D^b (Å)	d^c (Å)	θ^d (deg)
ortho-C−H···O	3.455	2.509	145.63
ortho-C−H···O	3.544	2.603	145.20
ortho-C−H···O	3.566	2.618	146.14
ortho-C−H···N	3.541	2.535	154.57
ortho-C−H···N	3.449	2.401	163.23
ortho-C−H···N	3.468	2.461	154.70
para-C−H···X[e]	3.556	2.699	135.96
para-C−H···X	3.924	3.289	118.67
para-C−H···X	3.968	3.341	118.24
meta-C−H···X	3.759	2.936	133.29
meta-C−H···X	3.805	2.994	132.27
$\pi\cdots\pi$[f]	3.301		

[a] All the C−H bonds are normalized to the standard neutron length (1.08 Å) along the C−H vector. [b] *D* is the distance between C and the acceptor (O, N, or ring centroid). [c] d is the distance between H and the acceptor (O, N, or ring centroid). [d] θ is the angle at H in C−H···X (X = O, N, or ring centroid). [e] Herringbone interactions are expressed as C−H···X, where X is the centroid of the aromatic ring acting as the C−H acceptor. [f] For $\pi\cdots\pi$ interactions, *D* is the perpendicular stacking distance.

The mean plane of the D_3−PU is almost parallel to (100) and makes an angle of 4.2° with it. A layered structure parallel to (100) arises from the "T"-geometry of the herringbone interactions between the phenyl groups (Figure 5, Table 2). All the *para* H-atoms on the phenyl groups and two of the *meta* H-atoms are engaged in these herringbone interactions and thus play a very important role in the generation of the trigonal layer structure.

The D_3−PUs are translationally stacked along [100] in an eclipsed manner and produce a columnar structure. Significantly, all the C−H···O bonds run in the [100] direction whereas all the C−H···N bonds run in the opposite $[\bar{1}00]$ direction. Since these C−H···O and C−H···N hydrogen bonded strands are polar, such translated stacking results in overall noncentrosymmetry with a macroscopic nonlinear coefficient one-tenth that of urea.[37] Three-dimensional structural control is a major endeavor in crystal engineering today, and it is realized here because the herringbone and hydrogen bonding interactions occur in roughly orthogonal directions (Figure 6). It may be noted that the D_3−PUs in **1** are only approximately D_3-symmetric and hence the network generated is quasi-trigonal and not perfectly trigonal. The supramolecular synthesis of octupolar network **A** (Figure 1) leading to the crystal structure of SHG active **1** underscores the importance of logic-driven supramolecular retrosynthesis in the quest for target networks with specific properties.

A comparison of the structure of **1** to that of *cis*,*cis*-cyclohexane-1,3,5-tris(α-picolin-6-yl)carboxamide, **9**, is perti-

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(33) (a) Terhune, R. W.; Maker, D.; Savage, C. M. *Phys. Rev. Lett.* **1965**, *14*, 681. (b) Maker, D. *Phys. Rev. A* **1970**, *1*, 923. (c) Clays, K.; Persoons, A. *Phys. Rev. Lett.* **1991**, *66*, 2980. (d) Kaatz, P.; Sheldon, D. P. *Rev. Sci. Instrum.* **1996**, *67(4)*, 1439.

(34) Platon-97: Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

(35) The X-ray diffraction on the crystals of **1** yielded an initial triclinic cell with dimensions $a = 6.601(2)$, $b = 12.426(6)$, $c = 12.649(4)$ Å, $\alpha = 118.23(2)$, $\beta = 97.93(5)$ and $\gamma = 101.22(3)^{\circ}$. The structure was solved and refined in the space group *P*1, with two molecules in the asymmetric unit. During the refinements two of the C-atoms became nonpositive-definite. It was identified from an analysis of the refined structure that the two symmetry independent molecules are stacked along [100] and they could be related by an *a*-glide perpendicular to [010]. This and the pseudohexagonal packing of the structure led us to search for the higher symmetry in the crystal. It was found that a higher symmetry space group is indeed possible, and this is the one reported in this paper.

(36) (a) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 290. (b) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (c) Steiner, T. *Cryst. Rev.* **1996**, *6*, 1.

(37) Details are provided in the section on NLO measurements.

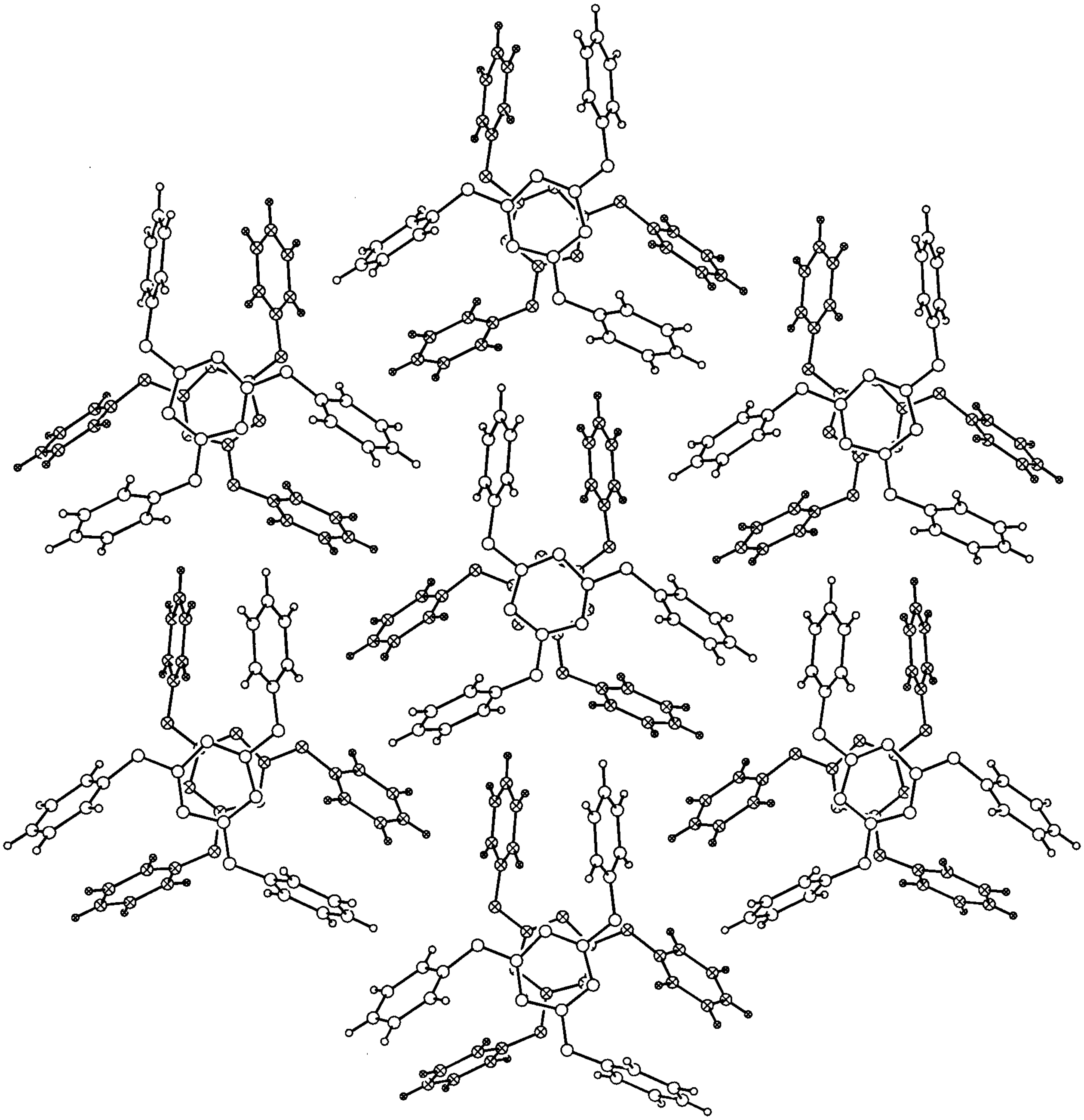
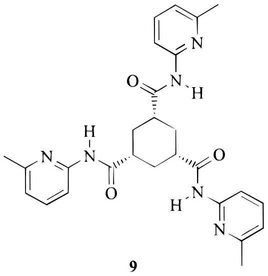


Figure 5. View down [100] showing the trigonal layer structure in **1**. Molecules at different heights along [100] are respectively unshaded and shaded. The packing of D_3−PUs within the layer is governed by herringbone interactions. The D_3−PUs are translation related along [001].

nent.[38] The structure of **9**, wherein successive molecules are interconnected by three N−H···O hydrogen bonds between amide functionalities, shows a supramolecular columnar structure similar to that found in **1**. In the noncentrosymmetric structure of **9**, the hydrogen bonds run along a polar direction (as they do in **1**); **9** has a trigonal octupolar network structure similar to **1**, and it has an SHG activity of 0.06 × urea. While the columnar structure in the triamide is stabilized by three strong (N−H···O) hydrogen bonds, the structure of **1** is stabilized by six weak (three C−H···O and three C−H···N) hydrogen bonds. Thus, we have serendipitously produced a C−H···O/C−H···N topological equivalent of an N−H···O based supramolecular structure. This indicates that when *weak hydrogen bonds are employed collectively they can work as effectively as their stronger counterparts.*



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The following points emerge from an analysis of the structure of **1**: (1) Such a compound may be a good starting point for producing PUs. (2) The aggregation of PUs is governed by a

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[38] Fan, E.; Yang, J.; Geib, S. J.; Stoner, T. C.; Hopkins, M. D.; Hamilton, A. D. *J. Chem. Soc., Chem. Commun.* **1995**, 1251.

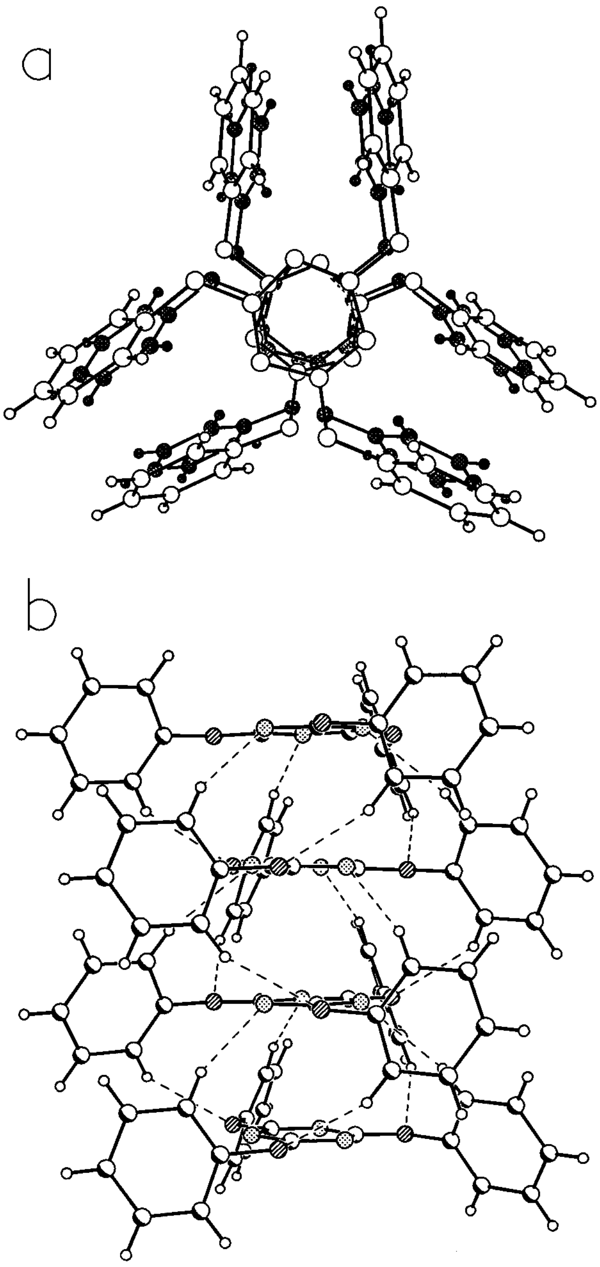

Figure 6. Two views of eclipsed stacking of D_3−PUs in **1**. (a) View down [100]. The unshaded D_3−PU is above the shaded one. (b) Side view of the same stacked pair of D_3−PUs. C−H···O and C−H···N bonds are indicated as dashed lines. The sense of these hydrogen bonds maintains the polarity. The shading scheme adopted is C − crescent, H − unshaded, N − dotted, O − hatched. The same shading scheme is followed in the remaining figures.

combination of $\pi\cdots\pi$ stacking and C−H···O/C−H···N interactions. The *ortho* H-atoms must be available as hydrogen bond donors. (3) The herringbone interactions are critical for the trigonal layer structure and involve participation of all the *para* and a third of the *meta* H-atoms. The trigonal network is thus expected to be the most sensitive to substitution in the *para* position. (4) The only site on the phenoxy group that appears not to disrupt formation of the D_3−PUs and the trigonal network is the *meta* position. Thus, we turned our attention to triazines **2**−**6**.

Table 3. Geometrical Parameters for Various Interactions Found in the Structures of **2**−**6**

		D_3−PU			C_{3i}−PU		
triazine	interaction[a]	*D*[b] (Å)	*d*[c] (Å)	θ[d] (deg)	*D*[b] (Å)	*d*[c] (Å)	θ[d] (deg)
2	*o*-C−H···O	3.655	2.682	149.64	3.344	2.685	118.96
	o-C−H···N	3.738	2.892	135.33	3.640	2.672	148.98
	p-C−H···X[e]	3.720	2.760	147.92			
	m-C−H···Cl	3.847	2.767	178.37			
	$\pi\cdots\pi$[f]	3.557			3.567		
3	*o*-C−H···O	3.636	2.644	152.50	3.373	2.668	122.42
	o-C−H···N	3.791	2.972	132.94	3.685	2.702	151.21
	p-C−H···X	3.835	2.846	153.10			
	m-C−H···Br	3.910	2.835	173.58			
	$\pi\cdots\pi$	3.620			3.618		
4	*o*-C−H···O	3.691	2.735	147.39	3.410	2.755	118.88
	o-C−H···N	3.727	2.829	140.64	3.689	2.726	148.64
	p-C−H···X	3.810	2.840	149.50			
	m-C−H···CH_3	4.160	3.230	178.96			
	$\pi\cdots\pi$	3.569			3.627		
5	*o*-C−H···O	3.850	2.853	152.53	3.600	2.837	127.66
	o-C−H···N	4.030	3.119	142.63	3.920	2.882	161.23
	p-C−H···X	4.049	3.038	156.03			
	Cl···Cl[g]	3.120					
	$\pi\cdots\pi$	4.025			3.948		
6	*o*-C−H···O	3.860	2.813	163.28	3.634	2.874	127.51
	o-C−H···N	4.022	3.106	143.00	3.945	2.934	155.91
	p-C−H···X	4.067	3.081	156.03			
	$CH_3\cdots CH_3$[h]	3.478					
	$\pi\cdots\pi$	4.029			3.970		

[a] All the C−H bonds are normalized to the standard neutron length (1.08 Å) along the C−H vector. [b] *D* is the distance between C and the acceptor (O, N, Cl, Br, methyl C-atom or centroid). [c] *d* is the distance between H and the acceptor (O, N, Cl, Br, methyl C-atom or centroid). [d] θ is the angle at H in C−H···X (X = O, N, Cl, Br, methyl C-atom or centroid). [e] Herringbone interactions are expressed as C−H···X, where X is the centroid of the aromatic ring acting as the C−H acceptor. [f] For $\pi\cdots\pi$ interactions *D* is the stacking distance. [g] For Cl···Cl interactions *D* is the distance between Cl-atoms. [h] For methyl−methyl close packing, the distance between two C-atoms of the interacting methyl groups is expressed as *D*.

Triazines 2−**4 Produce Perfectly Symmetric D_3−PUs in Their Crystal Structures.** The structures of 2,4,6-tris(3-chlorophenoxy)-1,3,5-triazine **2**, 2,4,6-tris(3-bromophenoxy)-1,3,5-triazine **3**, and 2,4,6-tris(3-methylphenoxy)-1,3,5-triazine **4** are discussed together because of their structural similarity. Triazines **2**−**4** crystallize in the trigonal space group $P\bar{3}c1$ (number 165) and are isostructural. The molecules lie on 3-fold axes, and D_3−PUs, assembled from two stacked molecules related by a 32-axis, are found in these structures (Figure 7a) as in **1**. Unlike the D_3−PUs in **1**, the PUs found in **2**−**4** maintain perfect D_3 symmetry. The two molecules in the D_3−PU are related by $\pi\cdots\pi$ stacking interactions of the central rings as well as by C−H···O and C−H···N hydrogen bonds. The geometrical parameters for various interactions found in these structures are given in Table 3. Each molecule in the D_3−PU donates and accepts three C−H···O bonds via one of the two symmetry independent *ortho* H-atoms. The same *ortho* H-atom is also involved in the formation of a longer, bifurcated[39] C−H···N hydrogen bond with the N-atom of the central triazine ring. Effectively, each D_3−PU is stabilized by stacking interactions and 12 weak hydrogen bonds, 6 C−H···O, and 6 C−H···N bonds.

The mean planes of the D_3−PUs in **2**−**4** are constrained by crystallographic symmetry to be parallel to (001). Unlike in **1** where three *para* and two *meta* hydrogen atoms are involved in herringbone intractions, only the *para* H-atoms are involved in **2**−**4**, and therefore the octupolar networks found in these triazines are ideally trigonal (Figure 8). This is reflected in their macroscopic, crystallographic 3-fold symmetry. Each D_3−PU

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[39] Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

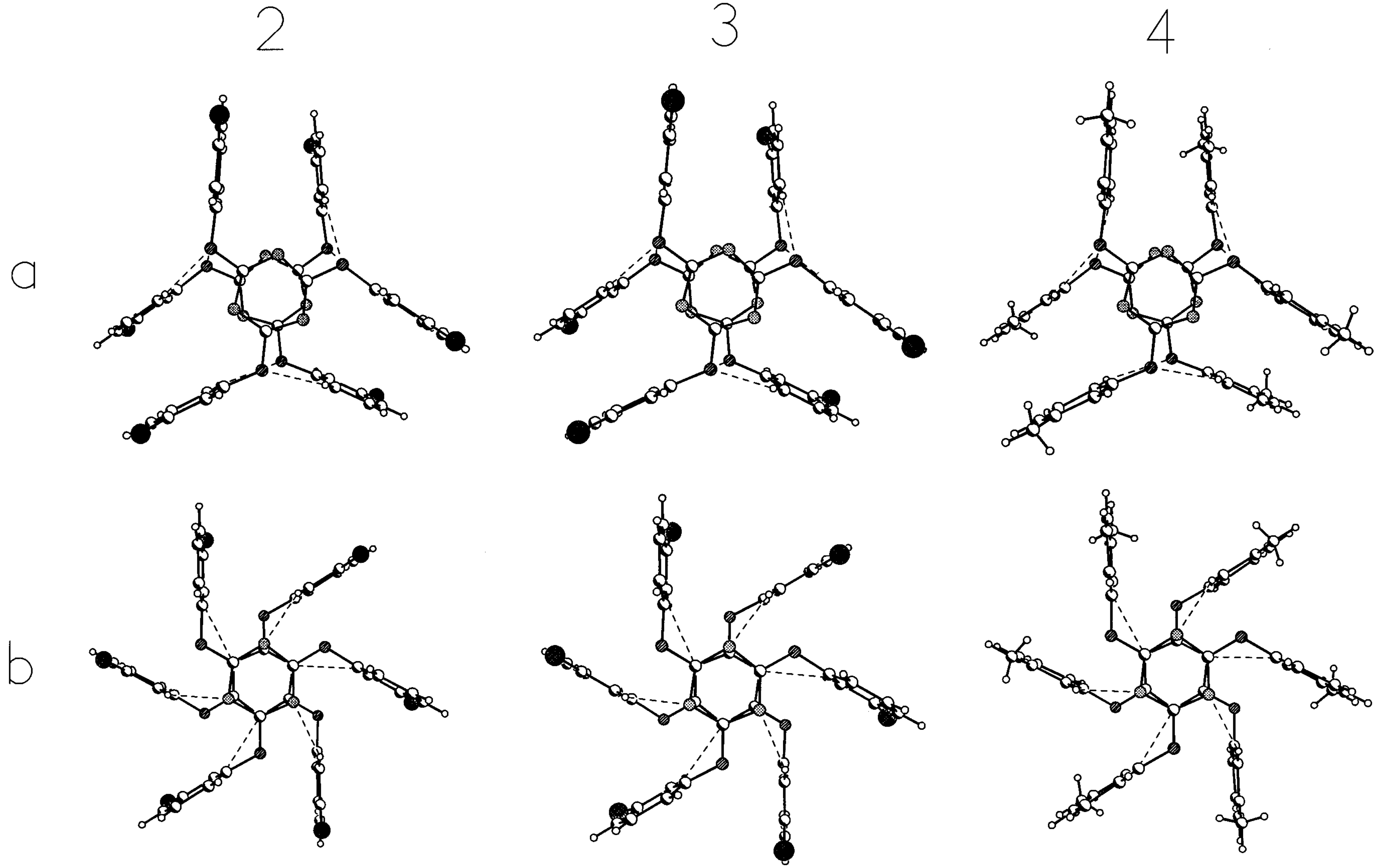

Figure 7. View down [001] showing the Piedfort units in **2**−**4**. (a) D_3−PUs. C−H···O bonds are indicated as dashed lines. (b) C_{3i}−PUs. C−H···N bonds are indicated as dashed lines. Bifurcation is shown in neither case.

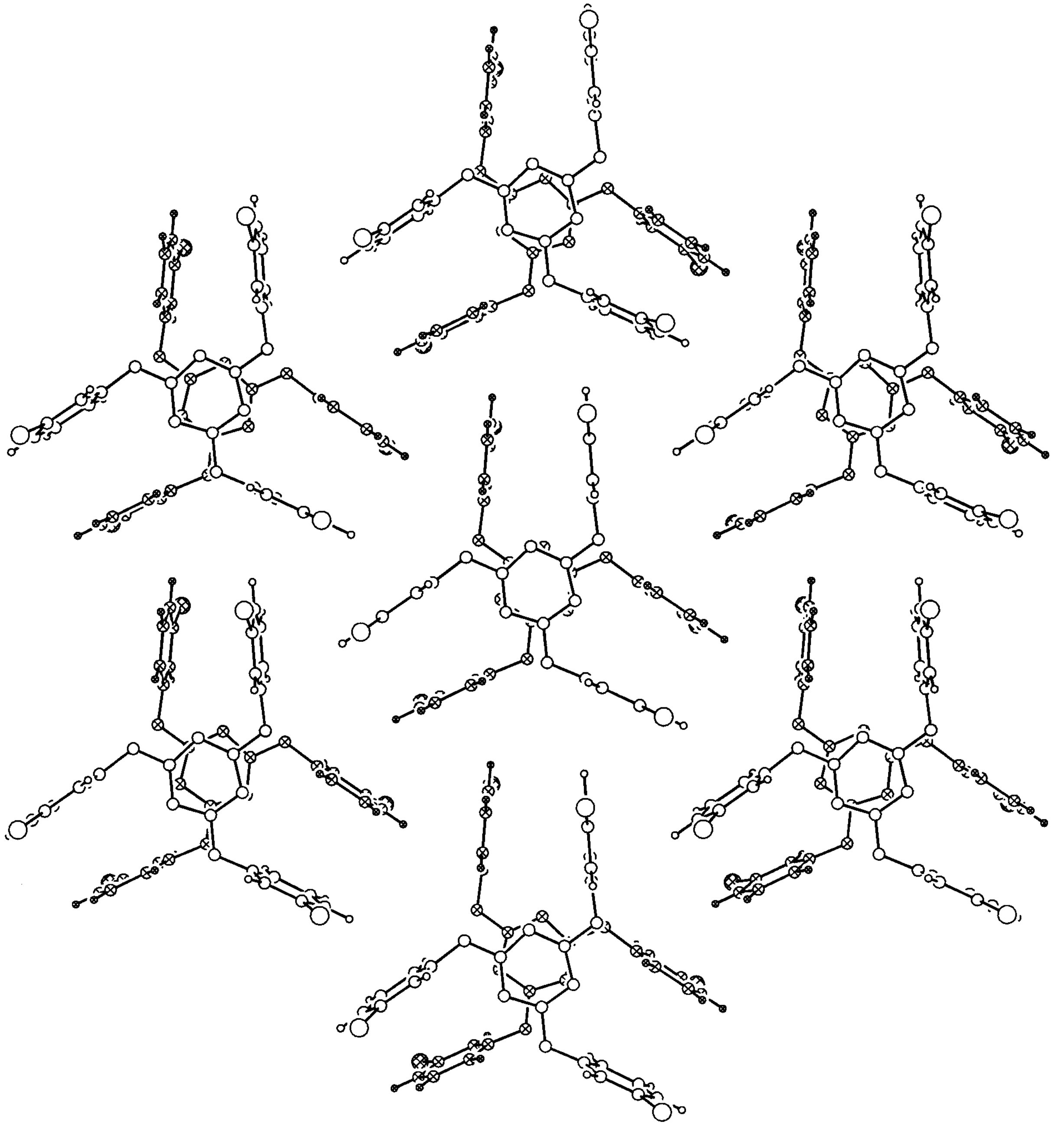

Figure 8. View down [001] showing the trigonal layer structure in **2**. Molecules at different heights along [001] are respectively unshaded and shaded. The packing of D_3−PUs within the layer is governed by herringbone interactions. The D_3−PUs are translation related parallel to (001). Contrast this with Figure 5.

in Figure 8 is connected to six neighbors within the layer through 12 herringbone interactions. Since the D_3−PUs in **2**−**4** are strictly D_3-symmetric, the trigonal network structure is also D_3-symmetric.[40]

The successive D_3−PUs in **2**−**4** stack along [001] in a staggered manner because eclipsed stacking, as in **1**, will lead to unfavorable steric interactions with the *meta* substituents. Two views of the staggered stacking of the $\bar{3}$ axis related D_3−PUs are shown in Figure 9. Such a staggered stacking of the D_3−PUs alleviates steric interactions between the bulky *meta* substituents on the phenoxy groups.[41] The isostructural nature of **2**−**4** illustrates the similar steric demand of chloro, bromo, and methyl groups. Incidentally, the staggered stacking of D_3−PUs defines a new PU with C_{3i} symmetry in these structures. Piedfort units of C_{3i} symmetry (C_{3i}−PUs) result if the lower molecule of the upper D_3−PU and the upper molecule of the lower D_3−PU are selected from a staggered stacked pair of D_3−PUs. Figure 7b shows the C_{3i}−PUs found in the structures of **2**−**4**.

The two $\bar{3}$-related molecules in the C_{3i}−PU are held by $\pi\cdots\pi$ stacking and also by C−H···O and C−H···N hydrogen bonds. One of the two symmetry independent *ortho* H-atoms is involved in bifurcated C−H···O and C−H···N hydrogen bonding between D_3−PUs. The other symmetry independent *ortho* H-atom on the phenoxy group is bifurcated between

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[40] A similar situation is observed in the structure of hexaphenylmelamine (Lindeman, S. V.; Shklover, V. E.; Struchkov, Yu. T.; Kuznetsov, S. N.; Pankratov, V. A. *Kristallografiya* **1982**, *27*, 65).

[41] Based on similar arguments Schwiebert et. al. have suggested in a recent paper (ref 2b) that chloro, bromo, and methyl derivatives of 2-benzimidazolones show offset stacking of tapes as opposed to perfect stacking of tapes in the unsubstituted hydrogen compound.

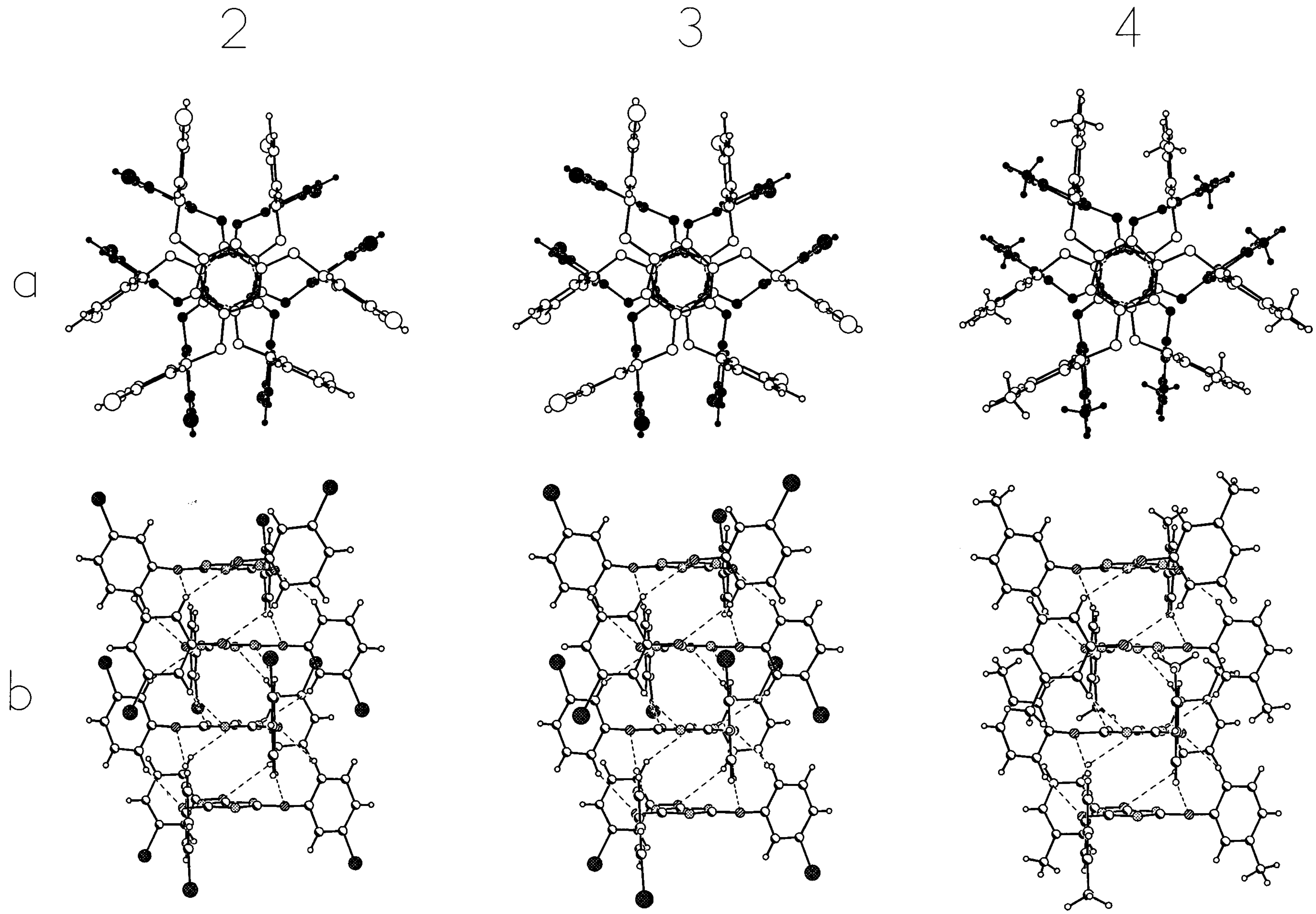

Figure 9. Two views of staggered stacking of D_3−PUs in **2**−**4**. (a) View down [001]. The unshaded D_3−PU is above the shaded one. (b) Side view of the stacked pair of D_3−PUs. C−H···O and C−H···N bonds are indicated as dashed lines. Contrast these with Figure 6.

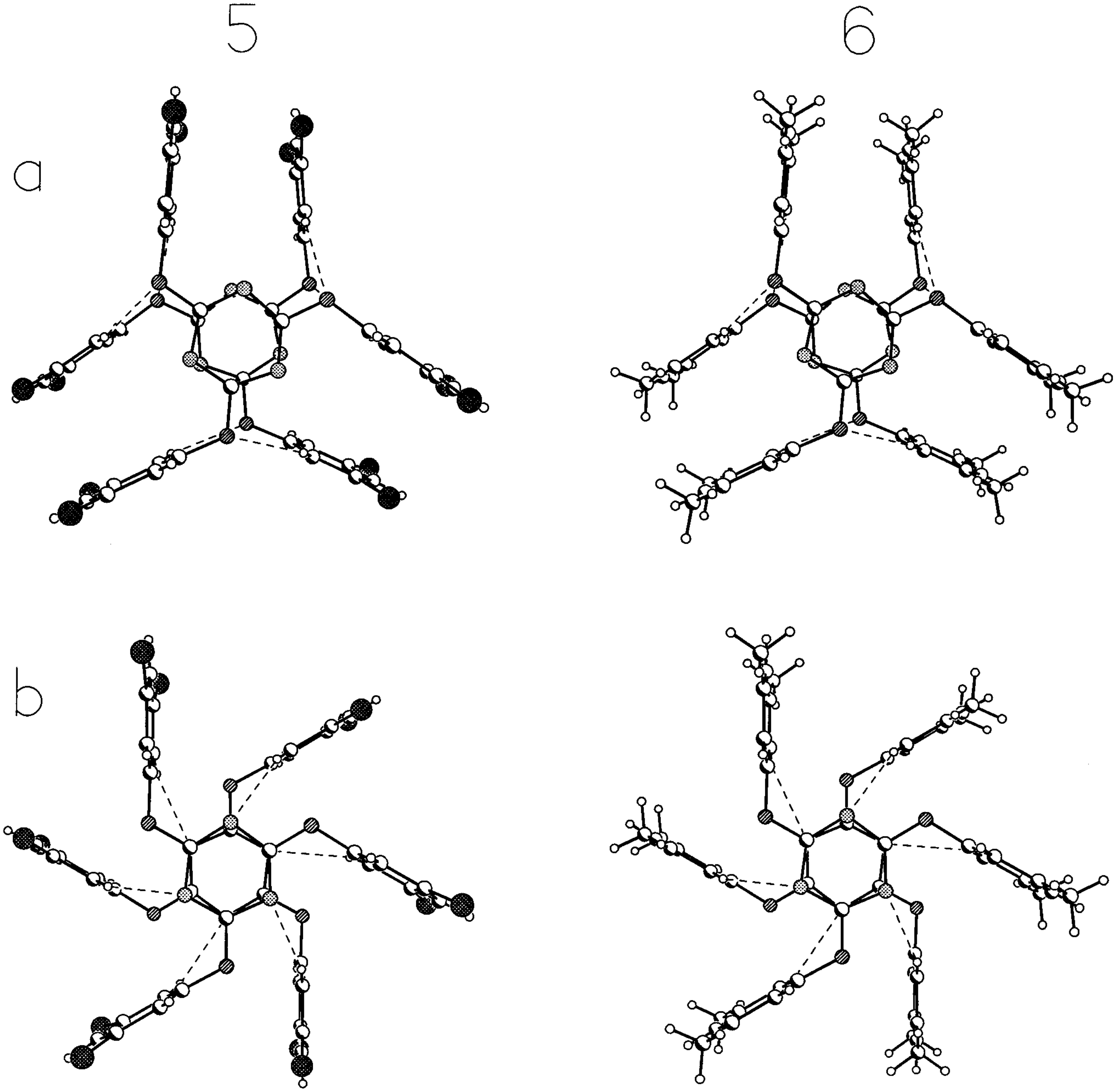

Figure 10. View down [001] showing the Piedfort units in **5** and **6**. (a) D_3−PUs. C−H···O bonds are indicated as dashed lines. (b) C_{3i}−PUs. C−H···N bonds are indicated as dashed lines. Bifurcation is shown in neither case.

C−H···O and C−H···N hydrogen bonds between the two molecules in the C_{3i}−PU. The data in Table 3 show that C−H···N bonds are relatively stronger than C−H···O bonds in C_{3i}−PUs, while the trend is opposite in D_3−PUs. Thus, the O- and N-atoms are responsible for effective hydrogen bonding in the alternating D_3−PUs and C_{3i}−PUs. In contrast we note that bifurcation is absent in **1** which has better C−H···O and C−H···N bonds.

The continuous, staggered stacking of D_3−PUs along [001] in **2**−**4** produces a supramolecular columnar structure wherein the C−H···O and C−H···N hydrogen bonded strands do not maintain structural polarity as in **1**. This is because the successive D_3−PUs are staggered such that inversion related molecules are stacked. Accordingly, successive trigonal octupolar layers are inversion related in **2**−**4**, and the structures are centrosymmetric.

Such stacking inversion could be a result either of attractive C−H···Cl/Br interactions or of the space filling demand of the bulky *meta* substituents. If attractive C−H···Cl/Br interactions are structure determining, the crystal structures of **2** and **3** should be different from the methyl derivative **4** because C−H···Me contacts are not attractive.[42] That **2**−**4** are isostructural and the fact that the intermolecular contacts are long (Table 3) indicates that layer inversion is a consequence of the similar space demand of the *meta* substituent.[43] To further examine the endurance of this structure type toward *meta* substitution, the structures of **5** and **6** were determined.

Chloro···Chloro and Methyl···Methyl Close Packing in the Structures of 5 and 6. The structures of 2,4,6-tris(3,5-dichlorophenoxy)-1,3,5-triazine **5** and 2,4,6-tris(3,5-dimethylphenoxy)-1,3,5-triazine **6** are isostructural to **2**−**4** and belong

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[42] Sarma, J. A. R. P.; Desiraju, G. R. *Acc. Chem. Res.* **1986**, *19*, 222.

[43] The corresponding fluoro triazine could not be crystallized for single-crystal X-ray analysis. Based on the powder X-ray spectrum of the material it was not possible to distinguish between noncentrosymmetric **1** and centrosymmetric **2**. However, the absence of a powder SHG signal suggests that it adopts a centrosymmetric structure.

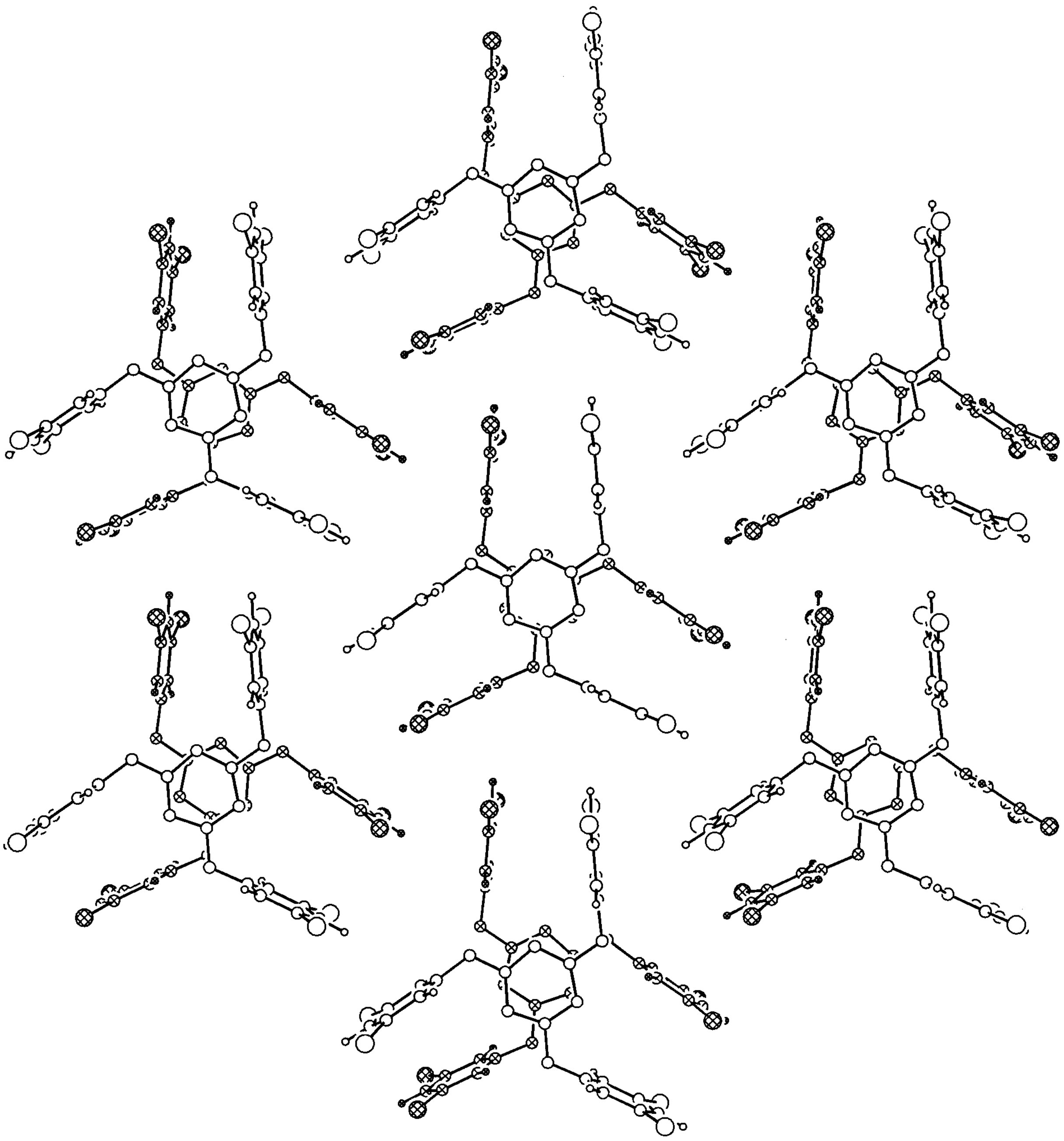

Figure 11. View down [001] showing the trigonal layer structure in **5**. Molecules at different heights along [001] are respectively unshaded and shaded. The packing of D_3−PUs within the layer is governed by herringbone interactions. The D_3−PUs are translation-related parallel to (001). Compare this with Figure 8.

to the same trigonal space group $P\bar{3}c1$ (number 165). In these structures too the triazine molecule sits on a 3-fold axis and D_3−PUs and C_{3i}−PUs may be identified (Figures 10 and 11). The $\pi\cdots\pi$ stacking separation and H···O/N distances in **5** and **6** are longer when compared with the corresponding distances in triazines **2**−**4** (Table 3). A supramolecular columnar structure is obtained by the staggered stacking of D_3−PUs along [001] (Figure 12).

The successive trigonal layers in **5** and **6** are inversion related and this reduces the repulsive interactions between the *meta* substituents. Interestingly in **5** the inverted layers are related by short Cl···Cl geometries between the two symmetry independent Cl-atoms (Cl···Cl: 3.12 Å). Usually, short Cl···Cl interactions have a structure influencing effect,[42,44] and in such cases the corresponding methyl analogue has a different structure.[45] When the Cl-atom merely has a space-filling role, the chloro and methyl groups (volumes: 20 and 24 Å^3, respectively) can be interchanged without much variation in the structure. That **5** and **6** are isostructural suggests that the chloro group is not involved in specific, attractive Cl···Cl interactions.[46] The short Cl···Cl separation in **5** is rationalized as a repulsive contact that is forced to accommodate itself within the extremely robust trigonal packing. This is corroborated by the almost linear C−Cl···Cl−C geometry (type I) and *not* the distinctive inclined geometry (type II) that is characteristic of the polarization induced and stabilizing Cl···Cl contact.[47]

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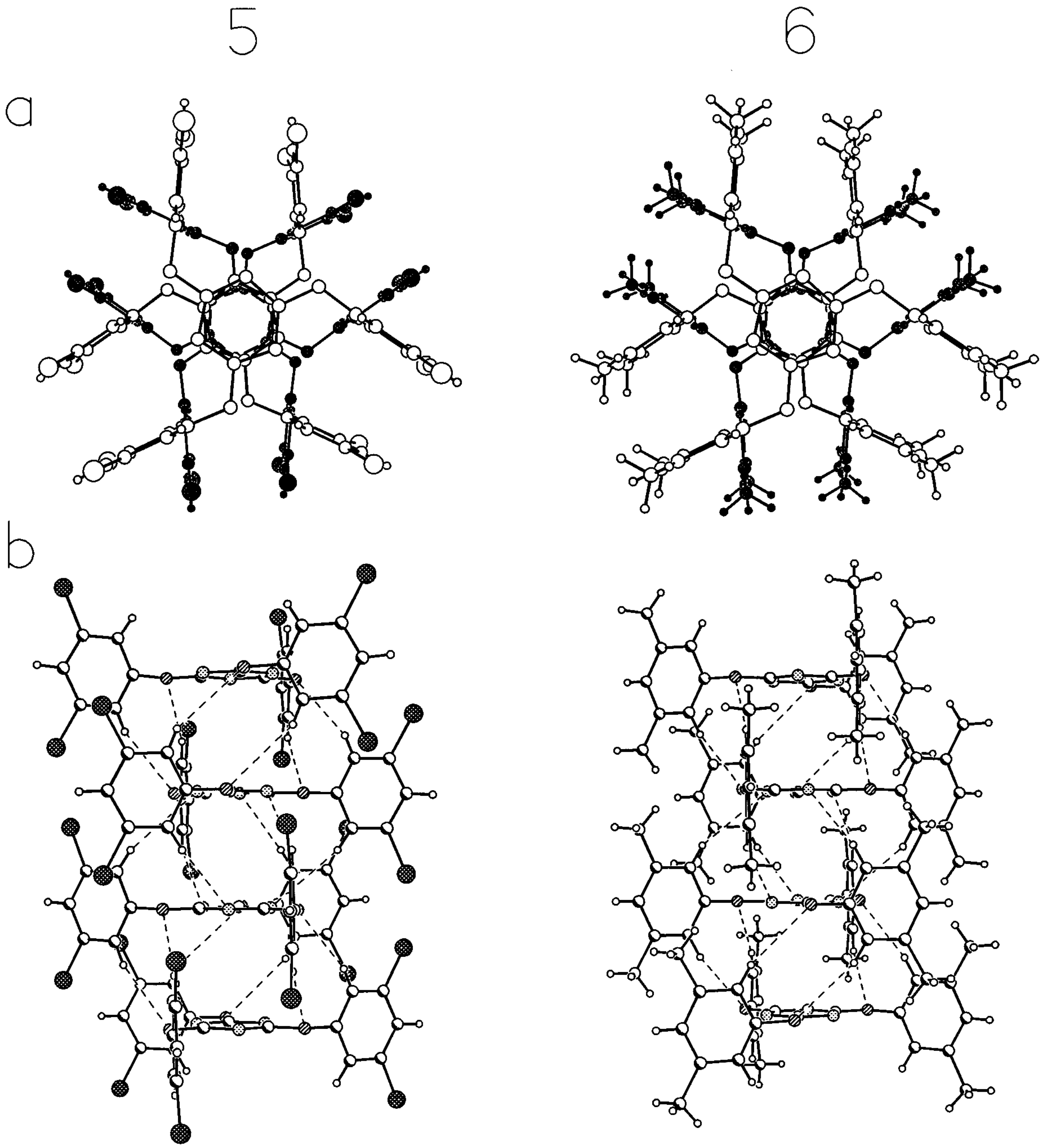

Figure 12. Two views of staggered stacking of D_3−PUs in **5** and **6**. (a) View down [001]. The unshaded D_3−PU is above the shaded one. (b) Side view of the stacked pair of D_3−PUs. C−H···O and C−H···N bonds are indicated as dashed lines. Compare this with Figure 9.

It is now instructive to compare the crystal structure of **1** with those of **2**−**6**. Triazine **1** yields a polar arrangement of monoclinic symmetry *Ia*. The molecules, with a chiral conformation in the crystal, are related by translation within noncentrosymmetric layers and are stacked along [100] and related by *a*-glide symmetry. Minor changes at the molecular level give **2**−**6** which yield noncentrosymmetric layers akin to **1**, but the molecules are stacked along [001] by $\bar{3}$ and 32 symmetry in the centrosymmetric space group $P\bar{3}c1$. Though **1** is monoclinic, it has quasi-trigonal octupolar layers comparable to the perfectly D_3-symmetric layers in **2**−**6** (compare Figures 5, 8, and 11). Herringbone interactions between the D_3−PUs in these layers are found in **1** as well as in **2**−**6**. The stacking distances vary linearly with size, and this is attributed to the space demand of the *meta* substituents: the shortest and the longest stacking distances are found in **1** and **6**, respectively (Tables 2 and 3). The similarities and differences between the network in **1** compared to those in **2**−**6** may be visualized by the stacked shaded−unshaded D_3−PU molecular diads in Figures 5, 8, and 11. While the herringbone interactions within and between the linear arrays are different in **1**, shaded-to-shaded and unshaded-to-unshaded within a linear array and shaded-to-unshaded and unshaded-to-shaded between the linear arrays (Figure 5) the interactions are all the same in **2**−**6**, always shaded-to-shaded and unshaded-to-unshaded (Figures 8 and 11). This differentiates the quasi and perfect D_3 symmetry of the trigonal networks in **1** and **2**−**6**, respectively. Two-dimensional supramolecular octupolar nonlinearities are well demonstrated in the structures of **2**−**6**, and all these triazines are excellent examples of two-dimensionally chiral systems.[24] The main difference between **1** and **2**−**6** lies in the mode of stacking of D_3−PUs: eclipsed stacking is observed in **1**, while staggered

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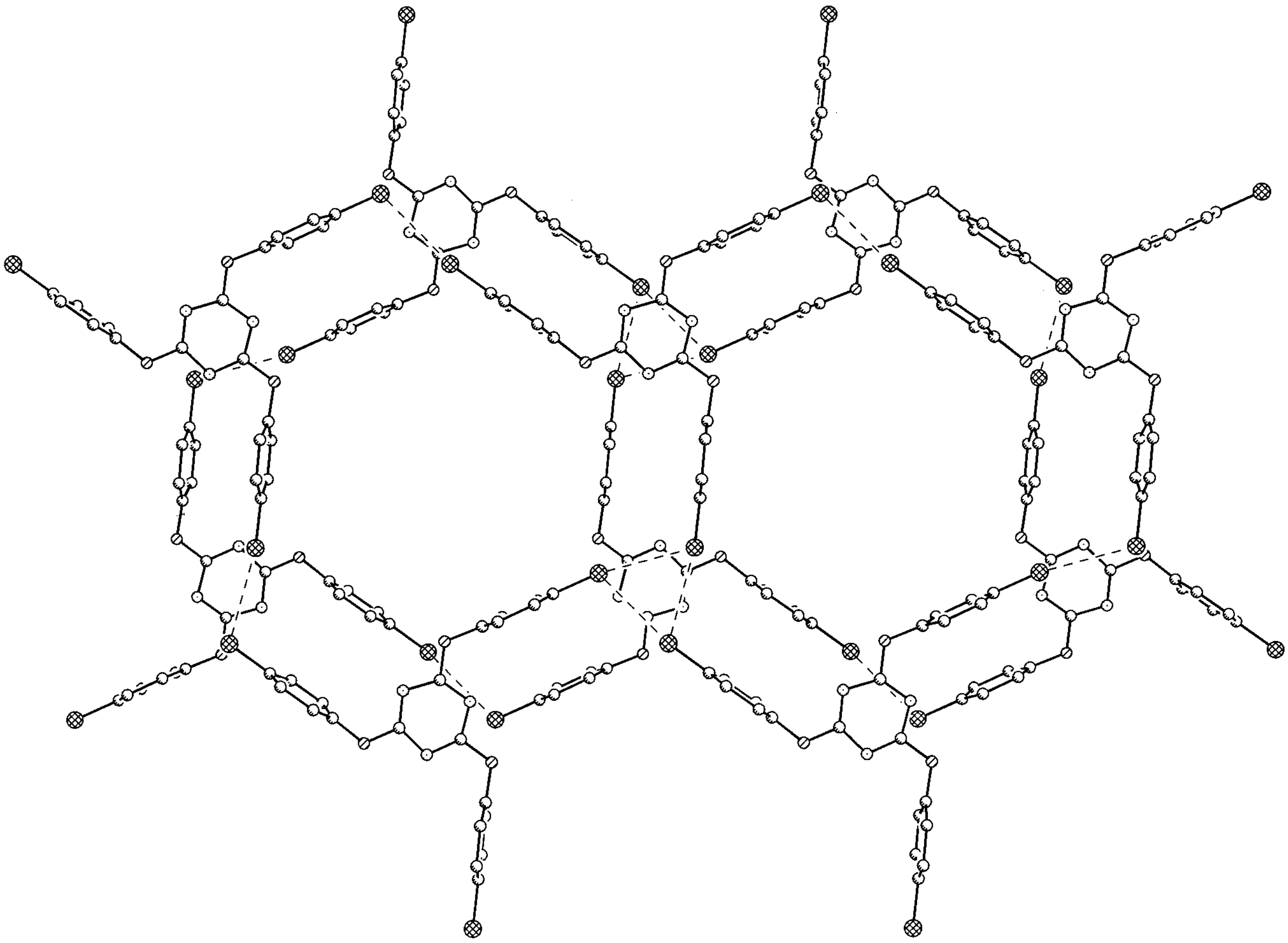

Figure 13. Hexagonal networks in the crystal structure of **7**. Notice that molecular synthons (triazine ring) and supramolecular synthons (Cl_3 trimer) alternate to produce the hexagonal sheet structure.

Table 4. Experimental Results at the Microscopic Level for Triazines **1**−**6** from Harmonic Light Scattering Measurements at 1.064 μm ($CHCl_3$)[a]

	1	2	3	4	5	6
$\sqrt{\langle\beta^2\rangle}(10^{-30}$ esu)	18 ± 2	19 ± 2	20 ± 4	15 ± 2	22 ± 5	21 ± 3
β_{yyy} (10^{-30} esu)	29.2	30.7	32.4	24.3	35.6	34

[a] The microscopic tensorial coefficients, β_{yyy} are deduced from these measurements.

stacking is observed in **2**−**6**. This leads to the following differences between the structure of **1** and those of **2**−**6**: (1) the absence and presence of C_{3i}−PUs, (2) the absence and presence of interactions between the *meta* substituents, (3) the absence and presence of inversion between layers, and (4) the presence and absence of bulk noncentrosymmetry.

Nonlinear Characterization of Triazines 1−**6 at the Molecular and Crystal Level.** The molecular nonlinear coefficients, $\sqrt{\langle\beta^2\rangle}$ of compounds **1**−**6** determined from HLS measurements at 1.064 μm are given in Table 4. The molecular hyperpolarizability of these compounds is of the same order of magnitude as that of the classical dipolar pNA molecule ($\sqrt{\langle\beta^2\rangle} = 10 \times 10^{-30}$ esu) implying that there is a comparable, moderately efficient charge transfer in these molecular structures. The depolarization ratio $D = \langle\beta^2{}_{ZXX}\rangle/\langle\beta^2{}_{XXX}\rangle$ is about 0.63 for the different triazines, and this confirms their octupolar symmetry since the calculated D value for pure octupolar symmetry is 0.67.[18] Assuming a planar octupolar structure for these compounds, the resulting β tensor components reduce to the two β_{yyy} and β_{yxx} coefficients with $\beta_{yyy} = -\beta_{yxx}$, y lying along one of the three charge-transfer axes. After isotropic averaging, the microscopic β_{yyy} values can be inferred from the orientational averaging relation[17g,18] $\langle\beta^2\rangle = 8/21\beta^2{}_{yyy}$ in the octupolar case (Table 4).

An estimation of the nonlinear efficiency of crystalline **1**, using the oriented gas model, was performed noting that it is the only compound in the series that crystallizes in a noncentrosymmetric structure. Triazine **1** exhibited a SHG powder signal measured as one tenth that of the urea powder signal. Triazines **2**−**6** that crystallize in centrosymmetric structures did not show any measurable SHG signal.

Change in Structure Type for the *Para*-Substituted 7. The similarity between the structure types exemplified by **1** and by **2**−**6** is the trigonal network stabilized by herringbone interactions between the *para* H-atoms and the phenyl rings. To better understand the role of the *para* H-atoms in establishing the trigonal networks, the crystal structures of triazines **7** and **8** were determined. 2,4,6-Tris(4-chlorophenoxy)-1,3,5-triazine, **7**, and 2,4,6-tris(4-bromophenoxy)-1,3,5-triazine, **8**, are isostructural and crystallize in the hexagonal space group $P6_3/m$ (number 176). Crystals of **7** and **8** grow as solvates from chloroform, dichloromethane, ethyl acetate, benzene, and toluene. However, they readily lose their solvent of recrystallization and become opaque when taken out of the mother liquor. Also, they could not be cooled without destroying them. The structural results at room temperature are of low accuracy, and the solvent molecule could not be located. Since **7** and **8** are completely isostructural, we report the structure only of **7**[48] and that too only in the context of demonstrating the structural sensitivity of the *para* position of the phenyl ring in this family of compounds.

The crystal structure of triazine **7** has large hexagonal cavities with a diameter of 14.25 Å (Figure 13). The *para* Cl-atom forms intermolecular contacts with two other symmetry related atoms through trimeric Cl_3 supramolecular synthons. These synthons are structurally equivalent to the well-known $(OH)_3$ trimer synthon.[49] Cl···Cl contacts have two preferred geometries, type I ($\theta_1 \cong \theta_2$) or type II ($\theta_1 \cong 180°$, $\theta_2 \cong 90°$) where θ_1 and θ_2 are the C−X···X angles.[50] While space filling type I contacts are found in the structure of **5**, the contact present in **7** corresponds to the polarization induced type II category.[47] The trimer X_3 synthon is cyclic, and each halogen is appropriately polarized, behaving both as a donor and an acceptor. Such cooperativity[39] effects could enhance the strength of the X···X interactions.[51] It is clear that adoption of a particular structure type in the triazine family is very sensitive to substitution at the *para* position on the phenoxy groups. So long as the *para* H-atom is intact, a robust polar trigonal layer results. A *para*-halogen substitution results in a hexagonal layer structure. In summary, the supramolecular retrosynthetic approach provides excellent structural control in two dimensions even as we realize that control in the third dimension still remains to be achieved in a general sense.

Conclusions

Current advances in crystal engineering and nonlinear optics show that the intersection of these fields constitutes a fertile area of research. In particular, this work shows that an octupolar NLO substance may be realized at the supramolecular level. Octupolar systems offer advantages over dipolar systems with regard to manipulation of packing characteristics because they can be expressed as higher-dimensional networks and as such a greater proportion of the structure is amenable to retroanalysis. We find here that the generation of a target supramolecular network may be achieved not only from a molecular species but also from a convergent, relatively small supramolecular species. Typical examples are the herringbone interaction-based-synthons in **1**−**6**. Keeping this template intact, both structural mimicry and structural diversity may be manipulated at will in this family of triazines.

At the outset, we have stated that contemporary crystal engineering can be motivated by strategic/methodological, aesthetic, or application-oriented concerns. And yet, these motivations stand in no real contradiction to each another. The present paper illustrates that rather than being in conflict, these three fundamental concerns can converge to yield a family of solids that has much potential for development as functionalized materials.

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Supporting Information Available: ORTEP diagrams and tables giving crystal data and structure refinement, atomic coordinates, isotropic and anisotropic displacement parameters, and bond lengths and angles for **1**−**6** (38 pages). See any current masthead page for ordering and Web access instructions.

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(48) Crystal data for **7**: Hexagonal, $P6_3/m$, $Z = 2$, $a = 15.364(3)$ Å, $c = 6.855(2)$ Å, $V = 1401.3(6)$ Å^3, $D_c = 1.092$ Mg m^{-3}, μ(Mo-K$_\alpha$) = 0.348 mm^{-1}, $F(000) = 468$, $T = 293$ K, $1.53 \leq \theta \leq 24.99°$, $-1 \leq h \leq 15$, $-18 \leq k \leq 1$, $-1 \leq l \leq 8$, 2352 measured reflections, 898 independent reflections, 58 variables, full-matrix least-squares refinement on F^2, $R = 0.1236$, $wR_2 = 0.3172$, GOF = 1.280, C, N, O, Cl anisotropic, H isotropic.

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