MOLECULAR ENGINEERING OF TRIGONAL OCTUPOLAR MATERIALS

BASED ON 2,4,6-*TRIS*-DIARYLAMINO-1,3,5-TRIAZINES

By

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Abstract: Molecular engineering of some 2,4,6-(substituted biarylamino)-1,3,5-triazines and crystal data belonging to the products 2,4,6-(*m,m'*-ditolylamino)-1,3,5-triazine, 2,4,6-(*p,p'*-ditolylamino)-1,3,5-triazine and 2,4,6-(phenyl-*p*-tolylamino)-1,3,5-triazine were reported. Retrosynthetic analysis of trigonal octupolar networks led to the identification of *tris*-substituted diarylamino-triazines as molecular analogs of Piedfort units formed by cofacial dimers of 2,4,6-triaryloxy-1,3,5-triazine molecules. Synthesis of mono and diarylamiono triazines is achieved by coupling of the corresponding anilines with cyanuric chloride. Synthesis of diarylamines exhibiting different functional groups on two phenyl rings is attempted; the successful attempt in the case of phenyl-*p*-tolylamine is described. All the crystals obtained so far belong to centrosymmetric space group $P2_1/c$. Though none of the molecules retain trigonal symmetry in the crystal structures, pseudo-trigonal assembly of molecules is identified in some cases. The assembly of molecules within the crystals results in columnar structures formed by C-H..N and C-H..π interactions.

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Introduction

Design and synthesis of organic materials exhibiting large second harmonic generation (SHG) for the applications in the field of nonlinear optics (NLO) attracted intense interest since Davydov and co-workers[1] reported strong SHG from organic compounds having electron donor and acceptor groups attached to a benzene ring in 1970. After screening a wide variety of substituted benzenes for their SHG activity they came to the conclusion that *dipolar* aromatic molecules possessing electron donor and electron acceptor groups resulted in large SHG activity due to the intramolecular charge transfer between the two groups with opposing electronic properties. It has become evident from this study that a π-conjugated system possessing electron donor and acceptor groups will exhibit strong SHG activity if it does not have an inversion center as represented in Figure 1. This symmetry restriction is imposed upon even order NLO effects (such as SHG); materials exhibiting odd order nonlinearities are not restricted by a center of symmetry.

Figure 1. Schematic representation of dipolar organic NLO materials.

It should be mentioned here that SHG activities of organic compounds were first reported in 1964 by Rentzepis and Pao[2] in 3,4-benzopyrene and Heilmer *et al*[3]. in hexamethylene-tetraamine. Since then, the field of nonlinear optics has emerged as a major area of research bringing together such faculties as physics, chemistry, and materials science towards applications in photonics[4-9] and optoelectronics.[7,10,11]

Nonlinear optical effects arise when an intense electromagnetic field (in general laser light) is illuminated on a material system. This intense radiation induces electrical polarization within the material that results in new electromagnetic fields altered in phase, frequency, or amplitude; that is, in optically nonlinear properties.

A relationship between the polarization (p) induced of a molecule and the applied electric field E of incident electromagnetic wave at frequency ω can be written by:

$$p(\omega)= \alpha\, E^1 + \beta\, E^2 + \gamma E^3 + \ldots$$

where $p(\omega)$ is the induced polarization in a microscopic medium (e.g., a molecule or ion) at laser frequency ω; α is the linear polarizability; β is the first hyperpolarizability; γ is the second hyperpolarizability; and E is the applied electric field component. Analogously, the macroscopic polarization (P) induced in bulk media under intense electromagnetic fields of a laser beam can be expressed in a power series as:

$$P(\omega)= \chi^{(1)}E^1 + \chi^{(2)}E^2 + \chi^{(3)}\, E^3 + \ldots$$

Here $\chi^{(1)}$, $\chi^{(2)}$, and $\chi^{(3)}$ are the first-, second-, and third-order NLO susceptibilities, respectively. The macroscopic second-order optical nonlinearities are related to their corresponding microscopic terms β as follows:

$$\chi_{IJK}^{(2)} = N\, \beta_{ijk}\, f_I f_J f_K$$

where N is the molecular number density, f is the local field factor due to intermolecular interactions, and ijk and IJK represent directions along molecular and macroscopic axes.

First NLO phenomenon was reported by Franken *et al.*[12] in a quartz crystal one year after

the first laser was developed by Maiman[13] in 1960. In the beginning, most interest in

NLO materials was focused on inorganic materials;[14-17] interest in organic materials

spurred after the work of Davydov *et al.*[1] on dipolar aromatic compounds. The major

advantage of using organic materials for NLO applications lies in the inherent flexibility

in their synthesis; a large number of compounds possessing a range of geometries and

functional groups can be readily made using well-established synthetic chemistry. It

should be noted, however, that organic materials, in general, have limited thermal and

electrical stability.

This work describes materials that are designed to exhibit second-order NLO effects;

higher order effects are difficult to measure because higher order susceptibilities are

usually several orders of magnitude smaller than lower order ones. Much of current

interest in NLO materials is focused on the second- and third-order effects.

Figure 2 shows a prototypical second order NLO effect.[18] When a noncentrosymmetric

material possessing second-order susceptibility ($\chi^{(2)}$) is illuminated with a laser light, the

output radiation contains waves of not just input frequency, but also doubled frequency.

This phenomenon is generally referred to as frequency doubling or SHG.
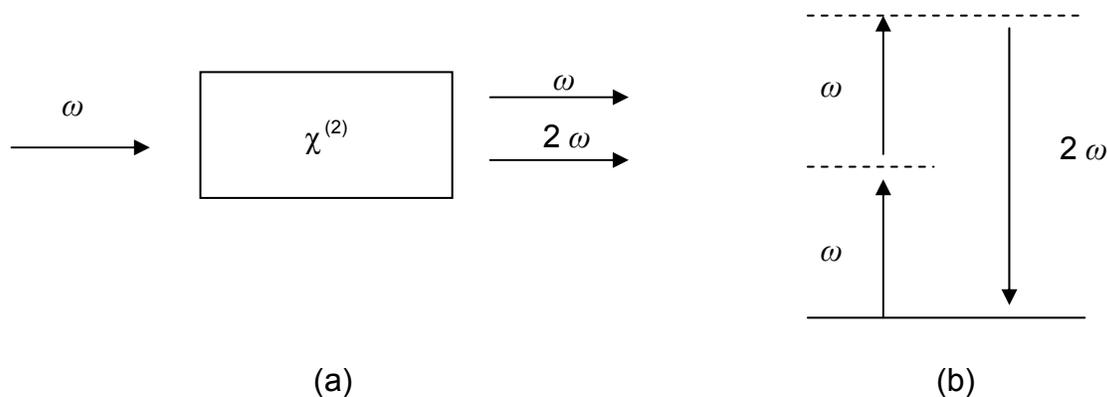
Figure 2. (a) Schematic representation and (b) energy-level diagram of SHG.

After the report of Davydov *et al.*[1] most of the interest in organic NLO materials was on *p*-nitroaniline-like[19] (*p*-NA) (Figure 3) dipolar organic NLO molecules. Today *p*-NA is accepted as the prototypical dipolar organic NLO material.

Figure 3. *p*-Nitroaniline (*p*-NA): prototype of a dipolar organic NLO molecule.

Even though dipolar organic NLO molecules exhibit large SHG activity, some problems concerning NLO applications have been identified: (a) problems during crystallization of long molecules; (b) problems in noncentrosymmetric self-assembly of molecules in crystals due to favored anti-parallel stacking; (c) limited electrooptic configurations due to high anisotropy in these molecules.

The second problem outlined above has been tackled in several ways such as introducing

directional hydrogen bonding interactions or chiral substituents. One eminent example

that uses a different strategy to generate acentric assembly includes POM (3-methyl-4-

nitropyridine-1-oxide)[20] (Figure 4); in this molecule the nitroxide and nitro groups exhibit

similar push-pull characteristics but the molecule as a whole shows significant β values,

and the material shows large $\chi^{(2)}$ values.
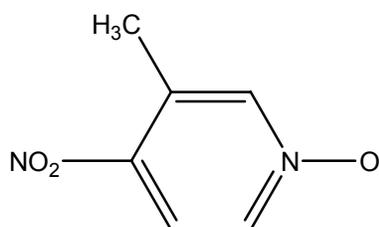
Figure 4. 3-Methyl-4-nitropyridine-1-oxide (POM).

Despite the progress made in the dipolar NLO, the dipolar molecules are not best-suited

for NLO applications since their high anisotropy does not provide polarization

independence.[21,22] Based on the experimental evidence[23] as well as on general tensorial

and quantum-mechanical considerations,[24] Zyss proposed that instead of dipolar

molecules more symmetrical molecules can self-assemble into more isotropic yet

noncentrosymmetric networks in two- and three-dimensions. He determined that these

molecules must have *octupolar* symmetry, and argued that these molecules can alleviate

the problems posed by dipolar molecules.[25]

Zyss also proposed that octupolar materials can be prepared through three important

routes[26-28]: (a) Guanidinium Route (e.g. Crystal Violet, Figure 5); (b) σ-linkage (e.g. Si);

and (c) TATB route (e.g. 1,3,5-triamino-2,4,6-trinitrobenzene, TATB, Figure 6).
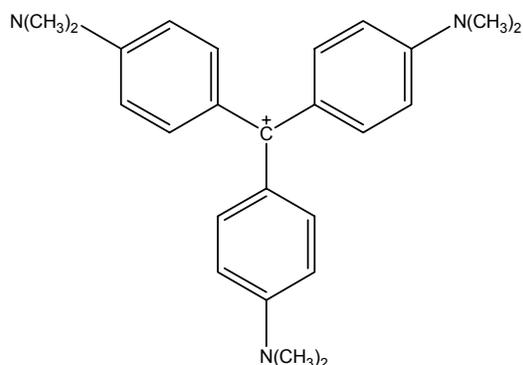
Figure 5. Guanidinium route
type octupolar
molecule: crystal violet.
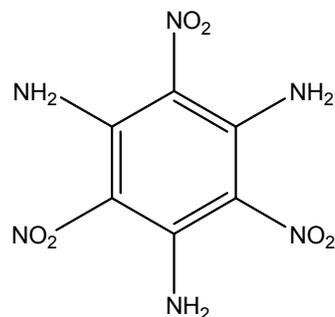
Figure 6. TATB route type
octupolar molecule
1,3,5-triamino-2,4,6-trinitrobenzene (TATB).

Since our interest is in "TATB route" type materials, it is represented schematically

(Figure 7). Molecular level octupoles are non-dipolar and non-centrosymmetric but one

has to ensure that noncentrosymmetric assembly is demonstrated in the crystal in other

words bulk noncentrosymmetry must be maintained. Octupoles show the polarization

independence and favor noncentrosymmetric assembly. Another advantage of octupoles

over dipolar molecules is that their β values increase as the extent of the charge transfer

increases, whereas in dipoles they increase to a maximum and then decrease as the bond-

length alternation increases.
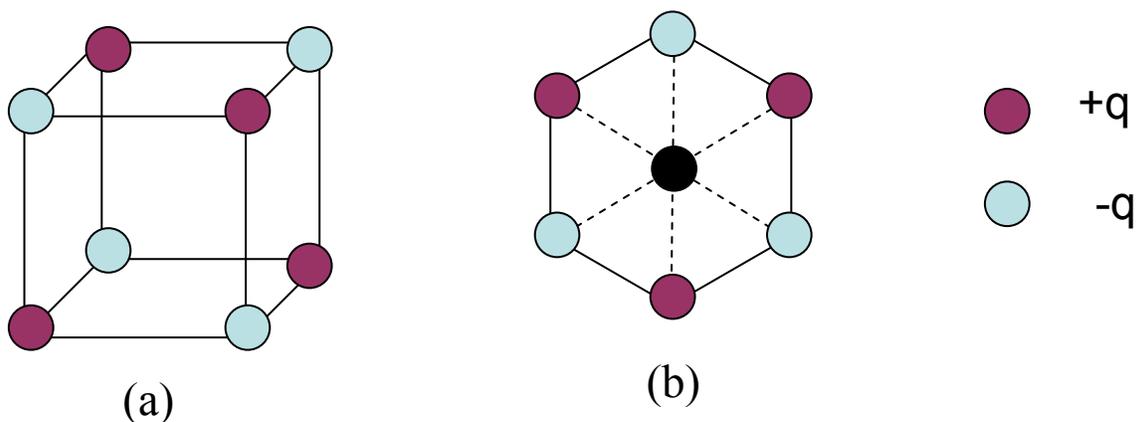
Figure 7. (a) Schematic representation of (a) idealized octupole represented as a cube with eight point charges. (b) Projection of the cube along a body diagonal transforms it to a two-dimensional trigonal symmetric material ("TATB route" octupole). The charges on the projected diagonal coincide and cancel out.

There are four factors affecting second-order optical nonlinearity:[29] (a) conjugation length; (b) strength of donor and acceptor groups; (c) nature of π-bonding sequence; (d) substitution. Therefore main work in organic octupolar NLO materials is centered on manipulating these four factors and further crystal engineering of such a molecule into a noncentrosymmetric network. To design such acentric network one can identify retrosynthetic routes as stated in the previous work reported by Thalladi *et al.*[30] It must be stated that following this trend is not trivial since majority of trigonal molecules routinely adopt close-packed crystal structures of low symmetry, according to Kitaiigorodskii's[19] theory of close-packing. Also today, the importance of H-bonding in crystal engineering is well known.[20] Hydrogen bonds can enforce a preferred orientation better than charge-charge or van der Waals interactions since they are moderately strong and directional.[21]

Etter has proposed the rules about the selectivity of different functional groups for hydrogen bonding.[22] Examples of hydrogen bonding making two-dimensional trigonal symmetric networks are shown below (Figures 8 and 9).
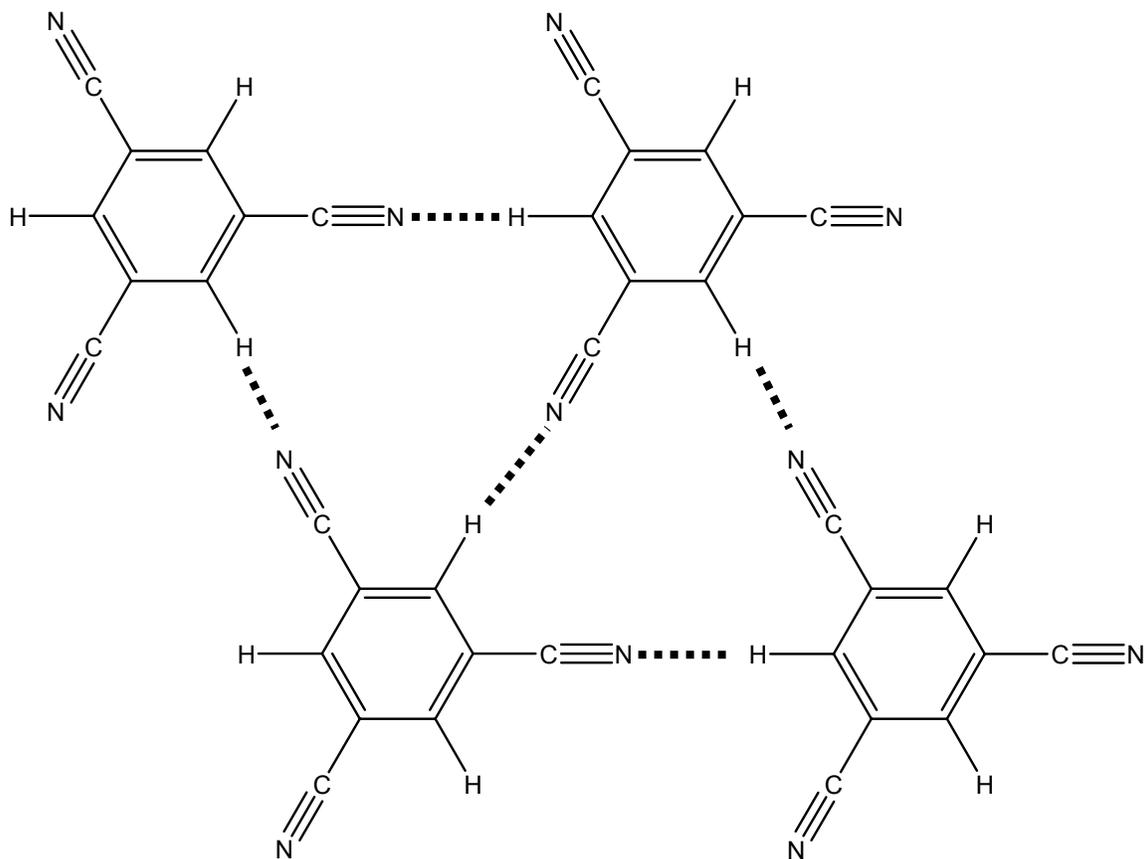
Figure 8. 1,3,5-Tricyanobenzene.
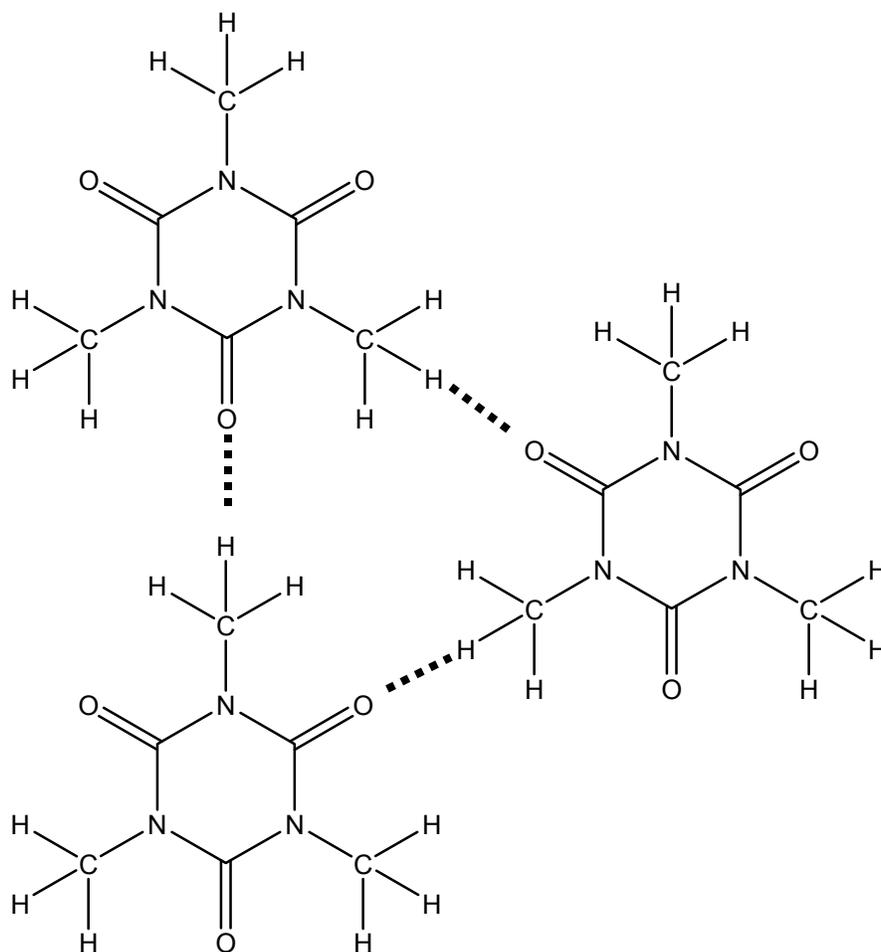
Figure 9. N,N,N-Trimethylisocyanurate.

Since three-dimensional structural control is difficult, we concentrated our interest in two-dimensional noncentrosymmetric networks. A typical symmetry pattern is that of trigonal molecules self-assembled into noncentrosymmetric structures as shown in Figures 8 and 9. When Thalladi *et al.* used retrosynthetic analysis of a two-dimensional noncentrosymmetric network **A** (Figure 10) to identify its structural units that are assembled with intermolecular interactions, they discovered the desired microscopic architecture **B**. They have identified crystalline triaryloxy substituted 1,3,5-triazines forming stacked diads called Piedfort units, as their starting supramolecular synthons **C**.

On the basis of expected specific electrostatic interactions between phenyl rings, by further retrosynthetic analysis they identified 2,4,6-triphenoxy-1,3,5-triazines **D** as starting molecules for the generation of noncentrosymmetric trigonal octupolar networks. In summary they reported crystal structures and NLO properties of molecules of a series 2,4,6-triaryloxy-1,3,5-triazines, **1-6** (Figure 11) that are stabilized by weak intermolecular interactions such as C-H…O and C-H…N hydrogen bonding.
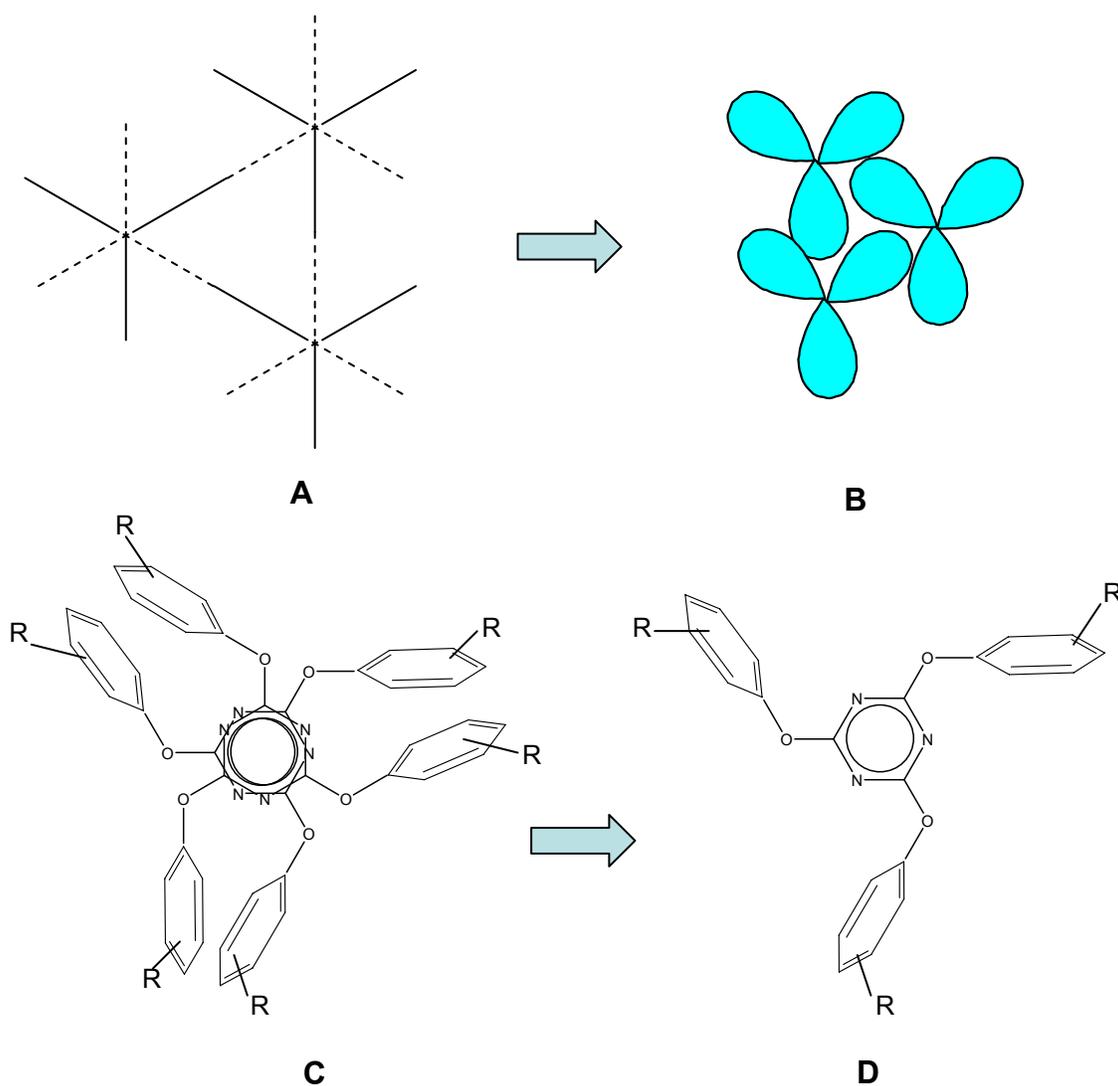
Figure 10. Retrosynthetic Analysis of trigonal octupolar network
(A) Trigonal network; (B) Recognition of trigonal species;
(C) Stacked molecular diads of triazines; (D) 2,4,6-triaryloxy-1,3,5-triazine.

R1

R3

R2

R2

R3

R1

O

N

N

O

N

O

R2

R1

R3

1 R1=R2=R3=H
2 R1=Cl R2=R3=H
3 R1=Br R2=R3=H
4 R1=CH$_3$ R2=R3=H
5 R1=R2=Cl R3=H
6 R1=R2=CH$_3$ R3=H
7 R1=R2=H R3=Cl
8 R1=R2=H R3=Br
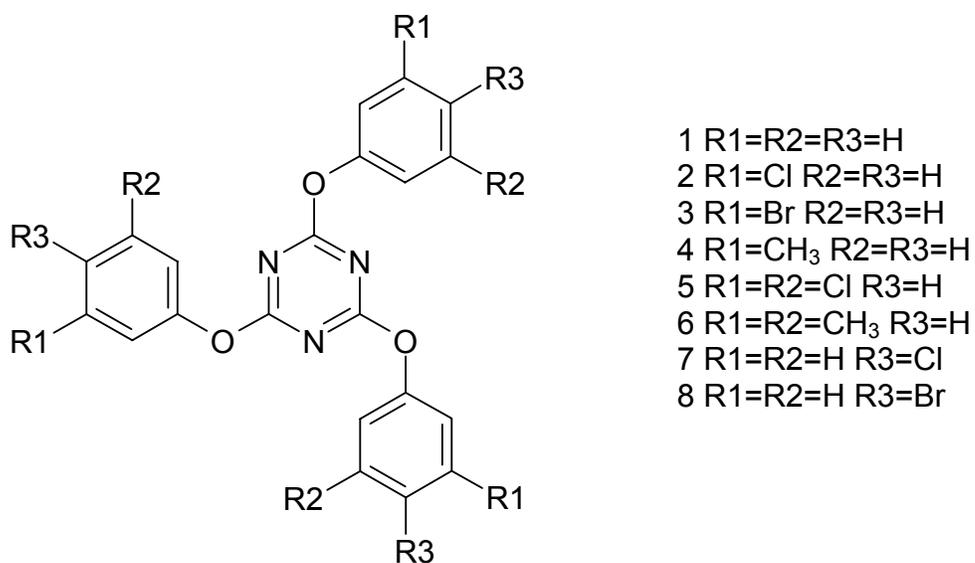
Figure 11. List of triazines studied by Thalladi *et al*.

In this work, based on the studies above, we proposed to create a molecular analog

(2,4,6-tris-(diphenylamino)-1,3,5-triazines) of the conceptual dimer formed from two

2,4,6-triphenylamino-1,3,5-triazines by stacking on each other.

Results and Discussion

In the area of trigonal organic octupolar NLO materials, most of the studies focused on the molecular level optimization, synthesis and characterization of the compounds. Both by experimental results and also theoretical calculations it has been verified that hyperpolarizability of an organic compound is related to several factors such as: 1) conjugation; 2) length of π-conjugation; 3) strength of electron donor and acceptor groups; and 4) substitution. Therefore, many researchers focused on the molecular level chemistry of trigonal organic compounds in by manipulating these four factors.

Figure 12 (below) shows some examples that belong to the trigonal octupolar compounds family. In molecular level they are all octupolar, noncentrosymmetric and show nonlinear optical properties. One important issue is to carry over this molecular noncentrosymmetry, to the bulk noncentrosymmetry, in other words to the supramolecular level.

(a)

(b)

R=4,4'-O(CH$_2$)$_{10}$-OC$_6$H$_4$C$_6$H$_4$CN

(c)

(d)
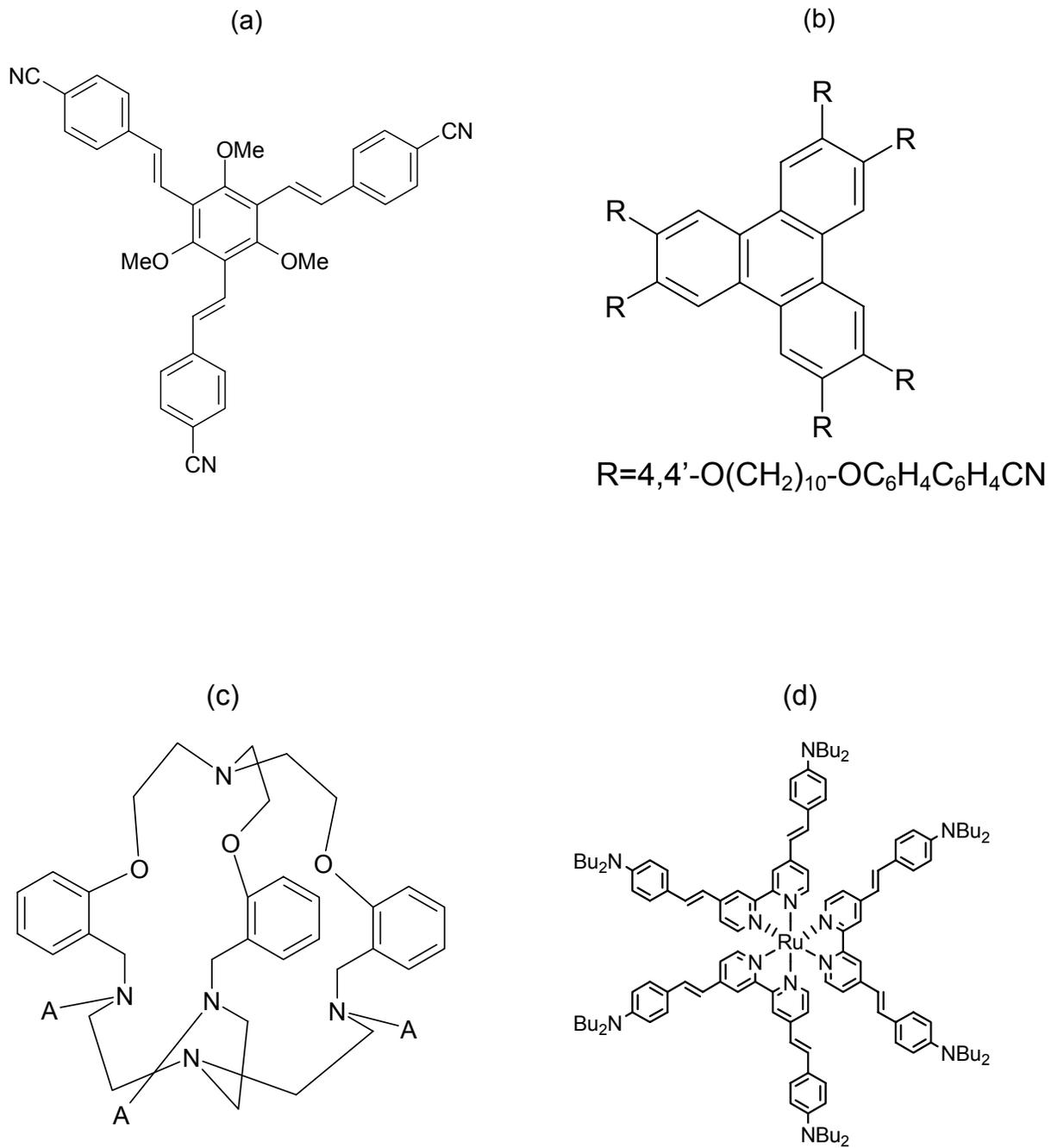
Figure 12. Examples of trigonal octupolar molecules.

Being octupolar, these molecules have a zero ground-state dipole moment, so they are

predicted to favor the formation of noncentrosymmetric networks.

Thalladi *et al*. reported a series of 2,4,6-triphenoxy-1,3,5-triazines (Figure 13). These

molecules are very good examples of molecular level design by using crystal engineering

principles to obtain octupolar NLO materials. This study is also a good example of how

to carry over molecular noncentrosymmetry into two-dimensional bulk

noncentrosymmetry in crystal structure, where compound 1 (Figure 13) adopts a

noncentrosymmetric crystal structure with a measurable SHG powder signal.

1 $R_1=R_2=R_3=H$
2 R1=Cl R2=R3=H
3 R1=Br R2=R3=H
4 R1=CH_3 R2=R3=H
5 R1=R2=Cl R3=H
6 R1=R2=CH_3 R3=H
7 R1=R2=H R3=Cl
8 R1=R2=H R3=Br
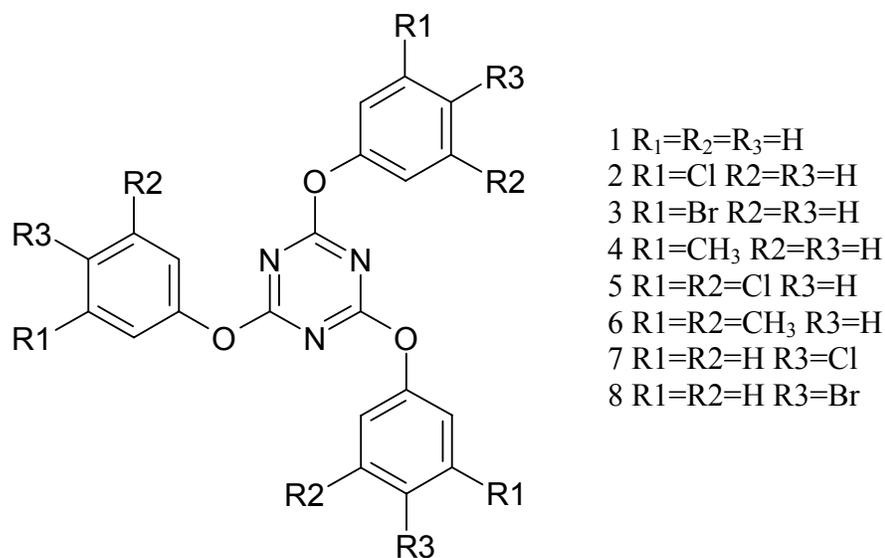
Figure 13. 2,4,6-Triaryloxy-1,3,5-triazines.

Using retrosynthetic analysis they identified appropriate precursor trigonal molecules (D)

(Figure 14) based on the concept of the dimeric Piedfort unit (C) where two TAOT

molecule are stacked on each other.
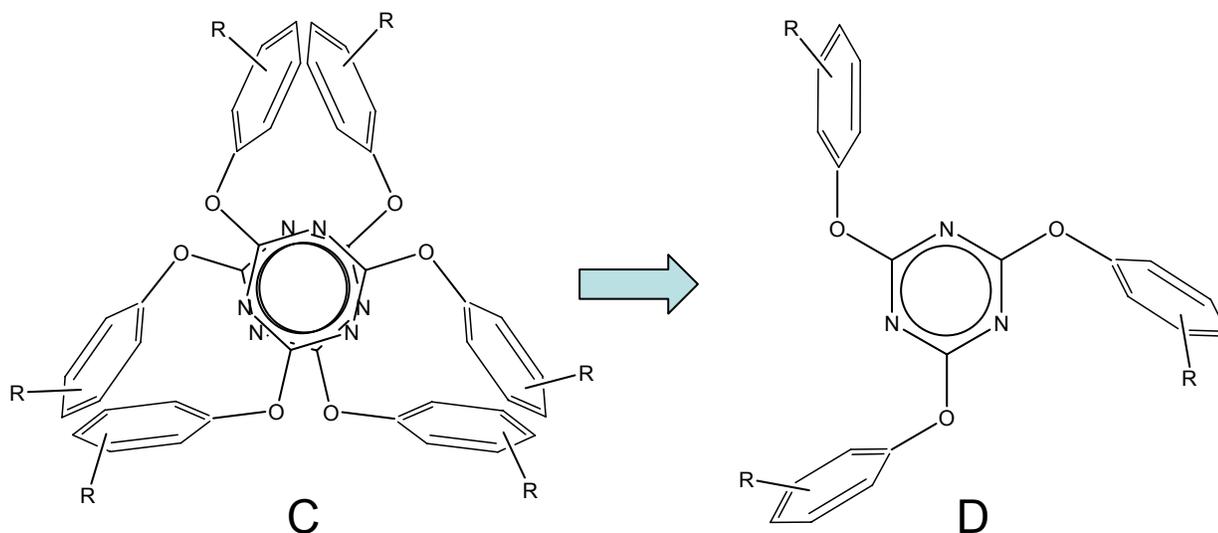
Figure 14. Retrosynthetic analysis of 2,4,6-triaryloxy-1,3,5-triazines.

In our work we intended to create molecular analogs of the conceptual dimer C that are optimized both at molecular and supramolecular level. It has been reported by Thalladi *et al.* that a typical symmetry pattern that leads to noncentrosymmetric two-dimensional networks can be developed by using molecules having trigonal symmetry as templates. We propose herein the retrosynthesis (Figure 15) of a two-dimensional network generated by the conceptual dimer through herringbone interactions between aryl rings. Further retrosynthesis let us identify tris-diarylamino-triazines as starting materials.

A

B

C
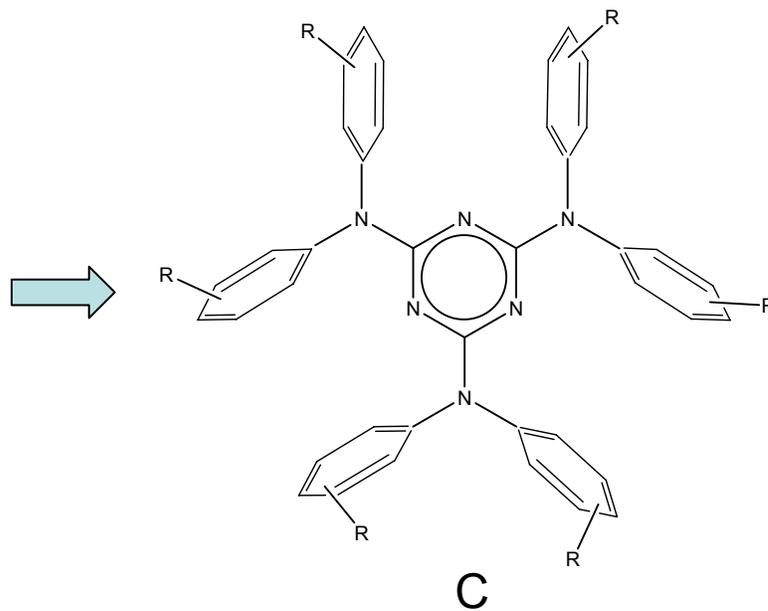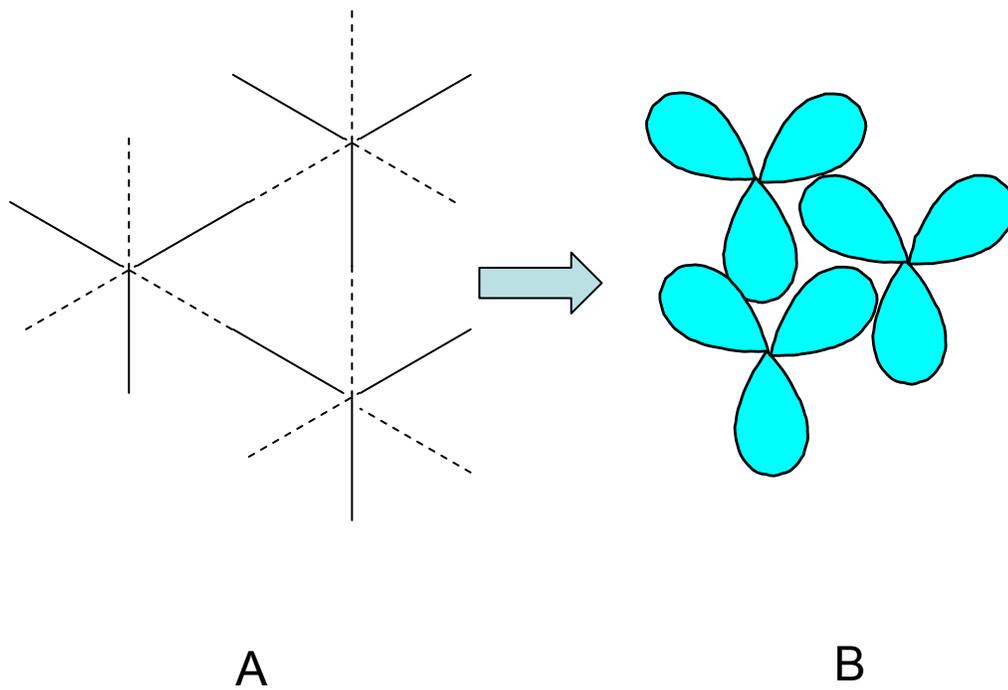
Figure 15. Retrosynthetic analysis for tris-diarylamino-triazines.

Our next goal was to synthesize this type of molecules and decide what type of R groups to use. We aimed at polar, nonpolar, mono substituted, symmetrical disubstituted (both R groups are same) and nonsymmetrically disubstituted (R1 and R2 are different) R groups to get different varieties and also to observe the effects of substitution and the effects of different R groups. Unfortunately, due to various constraints we were only able to synthesize few of them.

Attempted Synthesis of Diphenylamines

The best way to obtain the desired triazines is to couple cyanuric chloride with substituted diphenylamines. We began our work with an attempt to synthesize the desired diarylamines by coupling of aryl halides with anilines (Figure 16). Figure 17 shows the diarylamines we have been able to syntheisize; most of these were made only in small quantities due to a range of synthetic and purification difficulties described below.
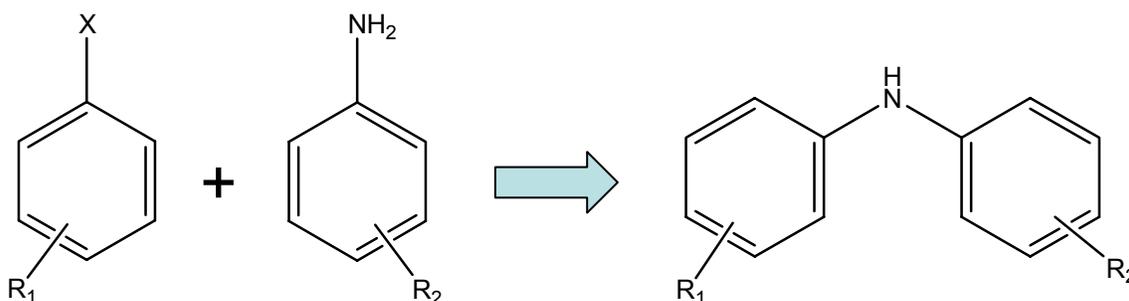
Figure 16. Schematic representation of synthesis of diphenylamines.

> *1)* phenyl-*p*-tolylamine
> 2) diphenylamine
> *3)* *N*-phenylpyridin-4-amine
> *4)* *p*-methoxydiphenylamine
> *5)* *p*-chlorodiphenylamine
> *6)* *p,p'*-dihydroxydiphenylamine

Figure 17. List of diphenylamines

There are many papers in the literature reporting the synthesis of substituted diphenyl amines; in general they follow the strategy (Figure 16) of using a mixture of catalyst, base and solvent. We used mostly the copper based catalysts; others used palladium or nickel with complex ligands and tedious reaction conditions. We attempted various conditions with copper catalyst by using copper iodide, copper sulfate or copper bronze, as well as changing base (K_2CO_3, $KO^{t}Bu$, KOH) and solvent. We also tried the synthesis in pressure vessels without any catalyst in the presence of potassium *t*-butoxide. It should be noted that for the mono-substituted diphenyl amines, there are two options: desired functional group can be either on aryl halide or on aniline, in particular for the synthesis of phenyl-*p*-tolylamine we tried the both ways. In addition, we attempted the synthesis of *p,p'*-dihydroxydiphenyl amine from the acid catalyzed condensation of *p*-aminophenol in the presence of benzenesulfonic acid. Unfortunately, most reactions resulted in low yields and many byproducts, except in the case of the phenyl-*p*-tolylamine.

Synthesis of Triarylamino-Triazines

Our aim was to synthesize tris-phenylamino-triazines and to use them as intermediates

for further synthesis of tri-substituted diarylamino-triazines, but we also considered the

opportunity to synthesize them as another family.

Synthesis of triarylaminotriazines can be achieved by coupling cyanuric chloride with

anilines (Figure 18). The anilines that were used are listed below (Figure 19), we also

tried some phenols (Figure 20) instead of anilines. In the case of 4-aminophenol and 3-

aminophenol, since they bear both amine and hydroxy functional groups, we found a way

in the literature to just react with amine group. We also tried to convert methoxy group of

the products 4-methoxyaniline and 4-methoxyphenol to hydroxy group using BBr_3.
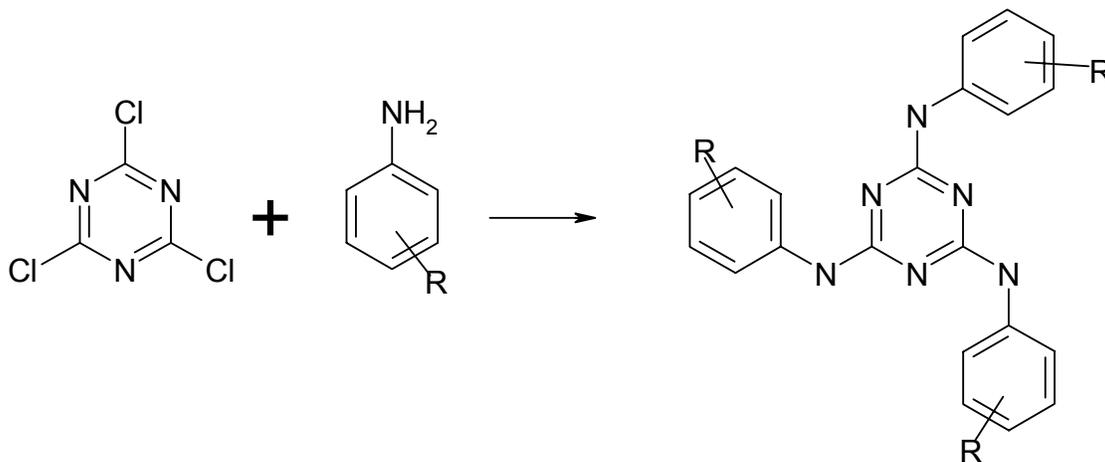
Figure 18. Schematic representation of synthesis of tris-substituted-triazines.

<table>
<tr><td>

1) Aniline
2) *p*-toluidine
3) *p*-chloroaniline
4) *p*-bromoaniline
5) 4-aminopyridine
6) 2-amino-5-methyl-aniline
7) *p*-amino-acetophenone
8) 3-chloro-4-methyl-aniline
9) 4-methoxyaniline

</td><td>

1) 4-aminophenol
2) 3-aminophenol
3) methoxyphenol
4) phenylphenol
5) *p*-cresol

</td></tr>
</table>

Figure 19. List of anilines.   Figure 20. List of phenols.

Synthesis of *tris*-Diarylamino-Triazines

Triazine family is well known in terms of synthesis. The reaction scheme (Figure 21) is similar to triarylaminotriazines: coupling of substituted diarylamine with cyanuric chloride at high temperatures (even though it is reported as first substitution occurs at 0 ^{o}C, second one at 25 ^{o}C and the third and last one at 67 ^{o}C, we got success over 200 ^{o}C) results in the formation of the triazine product with vigorous formation of HCl as the reaction progressed.
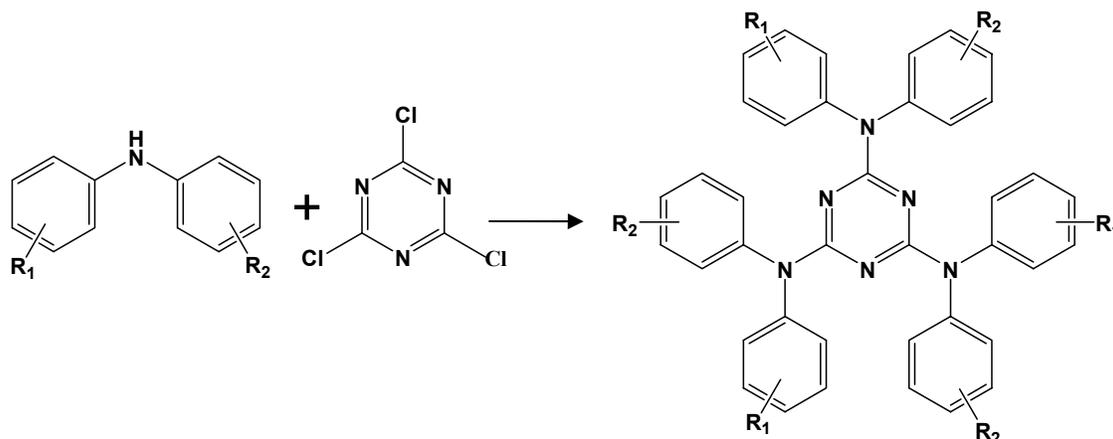
Figure 21. Schematic representation of synthesis of tris-diphenylamino-triazines.

Since our aim was both to synthesize triazines and also analyze the effects of substitution we decided to synthesize triazines with all kinds of functional groups, both symmetrical (R1 and R2 are same) and unsymmetrical (R1 and R2 are different). But due to some constraints we were only able to synthesize few of them, and they are listed below (Figure 22). Products 1-6 have been purified, the remaining ones are still in process.

 1) 2,4,6-(*m,m'*-ditolylamino)-1,3,5-triazine
 2) 2,4,6-(*p,p'*-ditolylamino)-1,3,5-triazine
 3) 2,4,6-(*p*-methyldiphenylamino)-1,3,5-triazine
 4) 2,4,6-(*m*-methyldiphenylamino)-1,3,5-triazine
 5) 2,4,6-(*p*-hydroxydiphenylamino)-1,3,5-triazine
 6) 2,4,6-(*m*-methoxydiphenylamino)-1,3,5-triazine
 7) 2,4,6-(*N*-phenyl-1-naphthylamino)-1,3,5-triazine
 8) 2,4,6-(*N*-phenyl-2-naphthylamino)-1,3,5-triazine
 9) 2,4,6-(*p*-nitrosodiphenylamino)-1,3,5-triazine
10) 2,4,6-(*p*-nitrodiphenylamino)-1,3,5-triazine
11) 2,4,6-(*m*-hydroxydiphenylamino)-1,3,5-triazine

Figure 22. List of tridiphenylamino-triazines obtained.

Crystallization

We tried to obtain crytals of the pure compounds by slow evaporation technique with different solvents. All crystals we got belong to the monoclinic space group $P2_1/c$. Even though they all belong to centrosymmetric space group, trigonal or pseudotrigonal symmetry can be seen in the crystal structures. All possible C-H..π interactions are listed in Table 1, C-H..N interactions are listed in Table 2, and also crystallographic data for the triazines 1-3 are listed in Table 3.

Table 1. Geometrical parameters for C-H..π interactions found in the structures of 1-3.

	H..Cg (A^o)	C..Cg (A^o)	C-H..Cg (^{o})
1	2.979	3.670	129.20
	2.855	3.509	125.57
	2.906	3.680	138.36
	2.768	3.717	170.63
	2.722	3.614	153.05
2	2.675	3.381	131.50
	2.979	3.715	135.24
	2.866	3.784	156.17
3	2.899	3.452	118.31
	2.647	3.482	146.82
	2.650	3.52	147.89

Table 2. Geometrical parameters for C-H...N hydrogen bonds in the structures of 1-3.

	H..N (A^o)	C..N (A^o)	C-H..N (^{o})
1	2.68	3.35	127
2	2.94	3.66	133
	2.96	3.69	134
	2.40	3.34	170
	2.66	3.52	150
3	2.87	3.63	137
	2.88	3.69	143
	2.49	3.40	160
	2.72	3.61	157

Table 3. Crystallographic Data for Triazines 1-3.

	1	**2**	**3**
Emp. Formula	$C_{45}H_{42}N_6$	$C_{45}H_{42}N_6$	$C_{45}H_{36}N_6$
Formula Wt.	666.85	666.85	624.77
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	p21/c	p21/c	p21/c
a (Å)	14.2520(18)	12.7264(3)	12.3563(8)
b (Å)	20.377(3)	25.8845(7)	24.1723(13)
c (Å)	13.7982(18)	11.3953(3)	11.5861(7)
α (deg)	90	90	90
β (deg)	113.493(2)	103.402(2)	102.021(4)
γ (deg)	90	90	90
Z	4	4	4
V ($Å^3$)	3674.5(9)	3651.58(17)	3384.7(4)
D_{calc} (Mg/m^3)	1.2054(3)	1.2130(1)	1.2261(1)

1. 2,4,6-(*m,m'*-ditolylamino)-1,3,5-triazine (MDMETZ)

This molecule has the formula $C_{45}H_{42}N_6$ and formula weight of 666.85. Crystal structure

belongs to the space group $P2_1/c$. We obtained the crystals from ethanol. Relevant

crystallographic parameters are listed in Table 3. As it can be seen from the picture

(Figure 23) the molecule does not retain trigonal symmetry in the crystalline form.
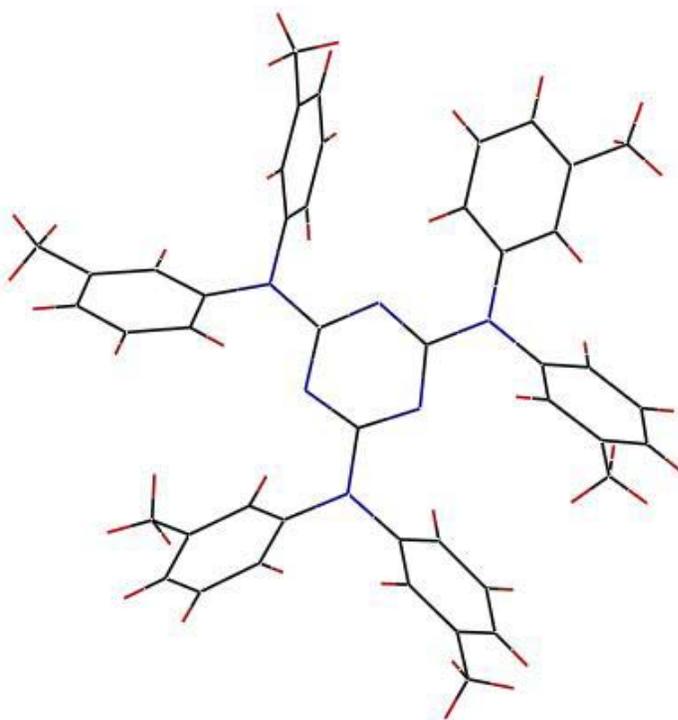

Figure 23. Picture of MDMETZ molecule in crystal.

Here phenyl rings are neither planar nor perpendicular to the central ring. Dihedral angles

between the planes belonging to phenyl rings attached to same nitrogen atom are given in

Table 4, and dihedral plane angles between the phenyl rings and central ring are given in

Table 5.

Table 4. MDMETZ dihedral angles between phenyl rings.

Cg	Cg	Alpha (^{o})
3	2	63.92
4	5	87.41
7	6	83.58

Table 5. MDMETZ dihedral angles between phenyl rings and central ring.

Cg	Cg	Alpha (^{o})
2	1	76.11
3	1	51.23
4	1	69.48
5	1	57.73
6	1	33.71
7	1	72.42

Figure 24 shows the arrangement of molecules within the crystal. To show the packing of

the crystals, pictures belonging to layers from all sides, view down [100] (Figure 25),

view down [010] (Figure 26), view down [001] (Figure 27) are shown in the following

pictures.
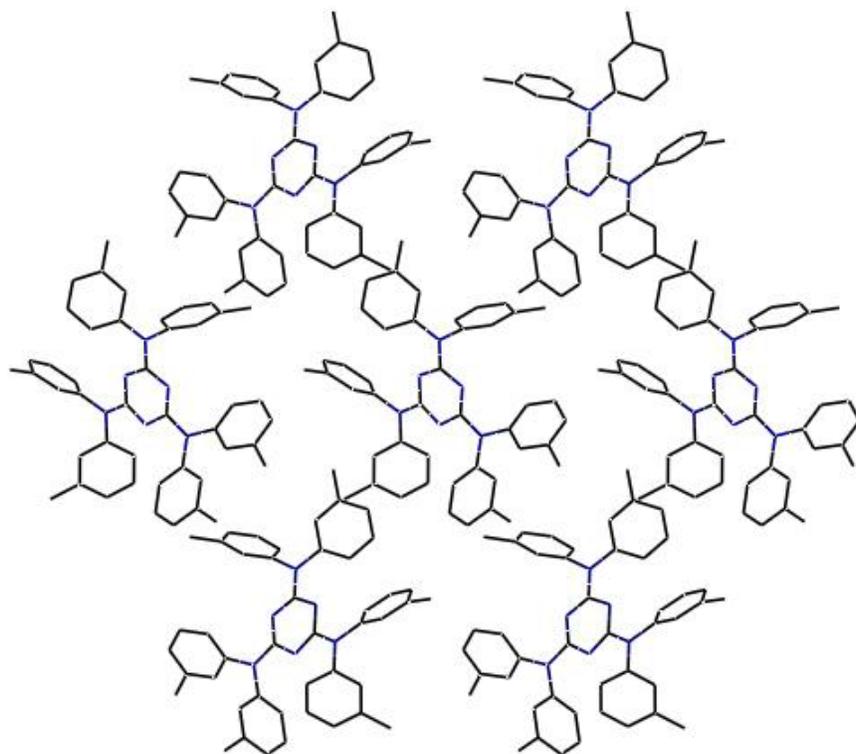
Figure 24. MDMETZ Hexagonal Structure.

Figure 25. MDMETZ crystal view down [100].
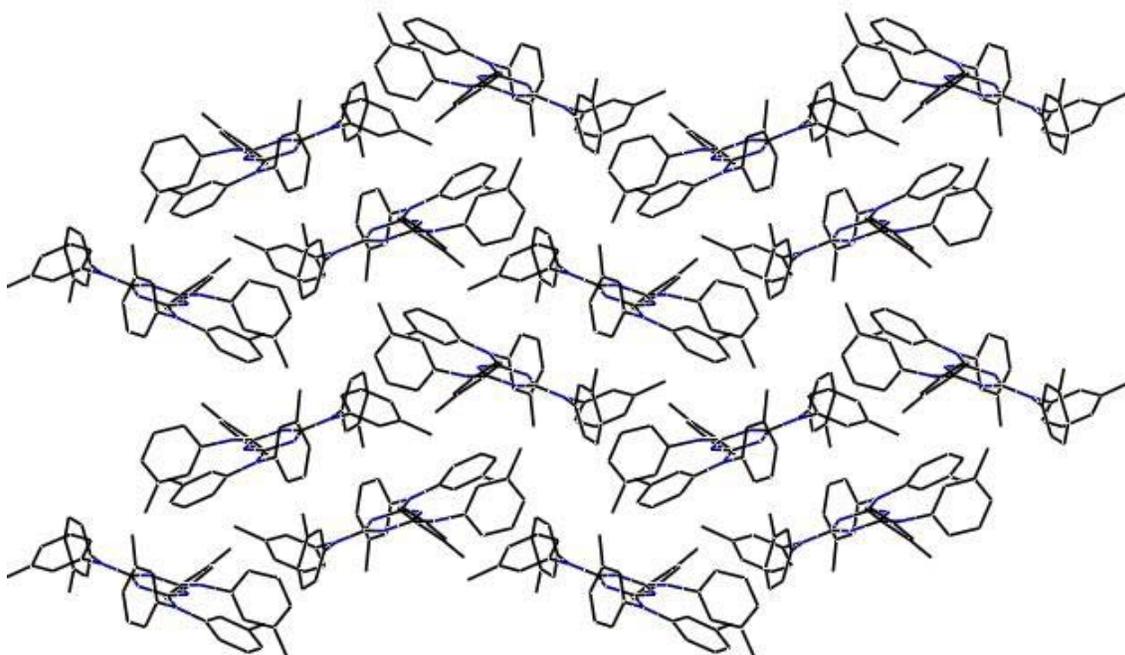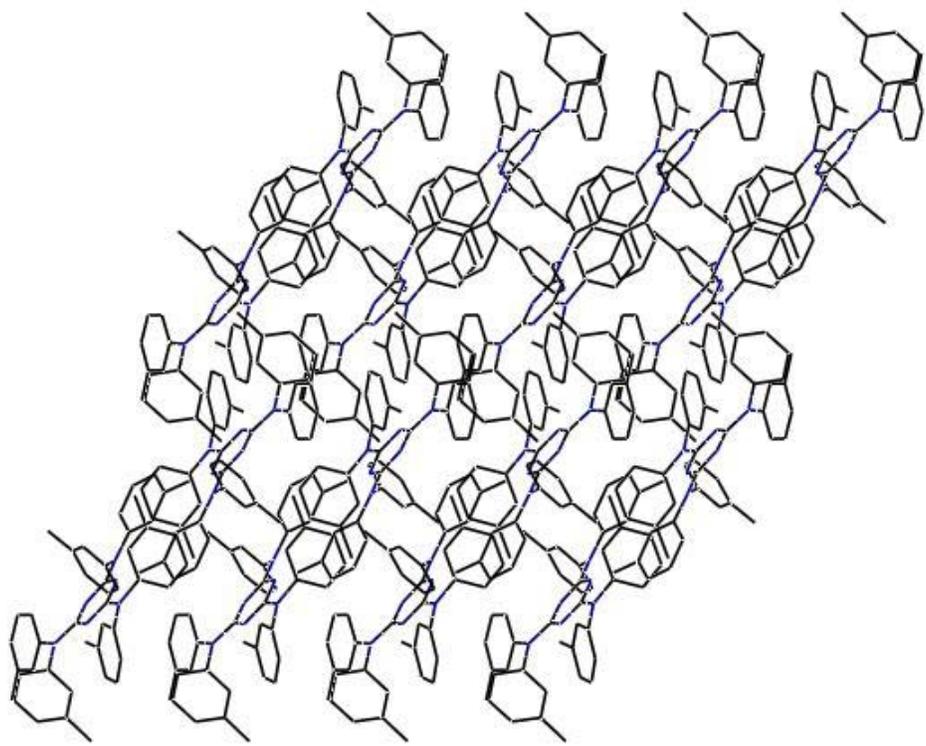
Figure 26. MDMETZ crystal view down [010].
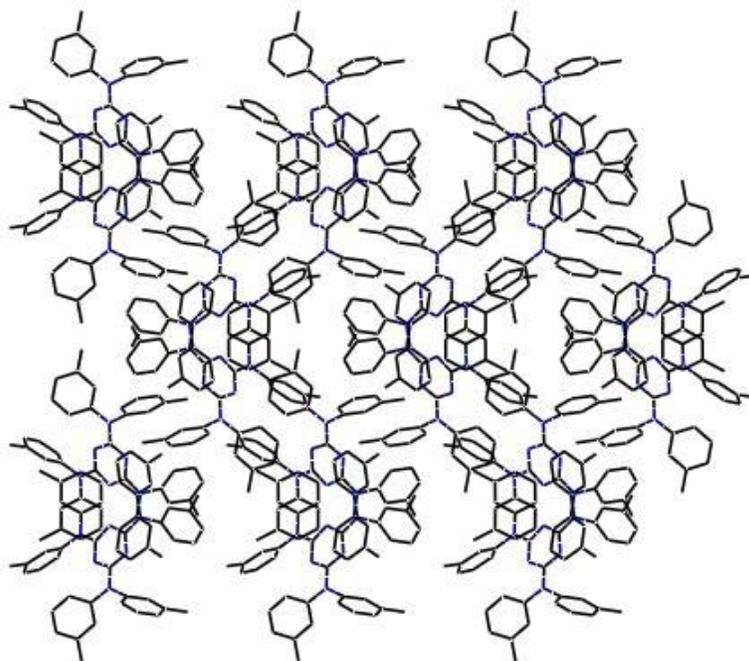
Figure 27. MDMETZ crystal view down
[001].

As shown in Figure 28, each MDMETZ molecule participates in two C-H…N contacts
and four C-H...π interactions. It should be noted that from this figure only two of the four
C-H...π can be seen . C-H..N interactions are shown in blue and C-H…π interactions are
shown in red color.
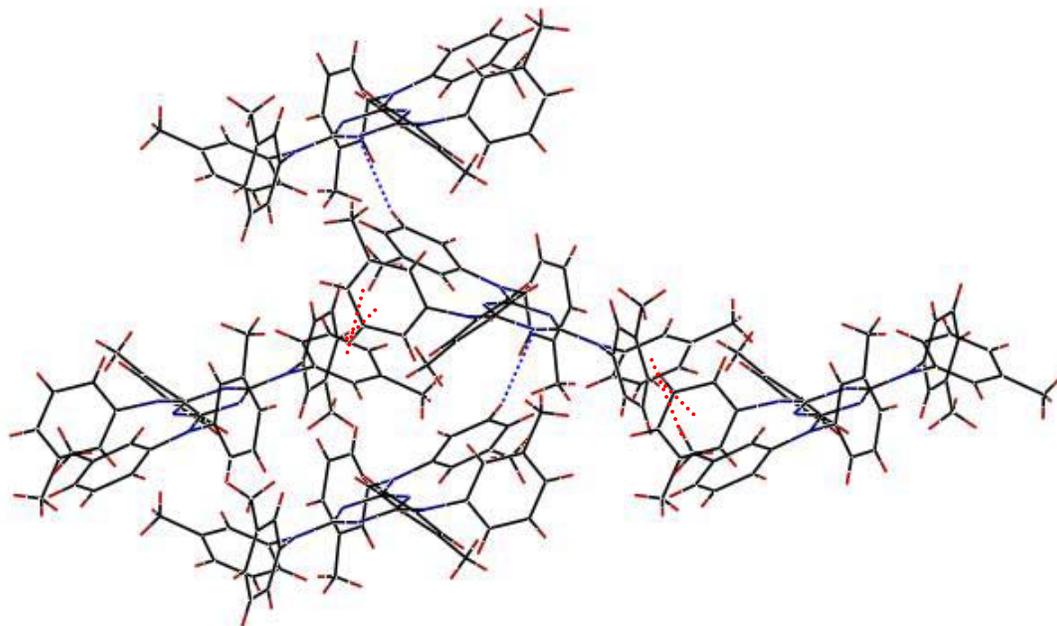
Figure 28. MDMETZ interactions view down [100]
(C-H..N:blue; C-H..π: red).

Below is the picture of the molecules that are connected by C-H...π bonding view down [001] (Figure 29). Central molecule is related to the other four molecules by screw axis. Even though it looks like they are all in the same plane, planes belonging to the central rings of the central molecule and others are creating a 31-degree angle. In the plane of paper, view down [100], they are all connected to one molecule above and one molecule below by C-H..N H-bonding (can be seen from Figure 25). Also the angle between the central molecule and the others and the zig-zag shape of the layer can be seen in same picture.
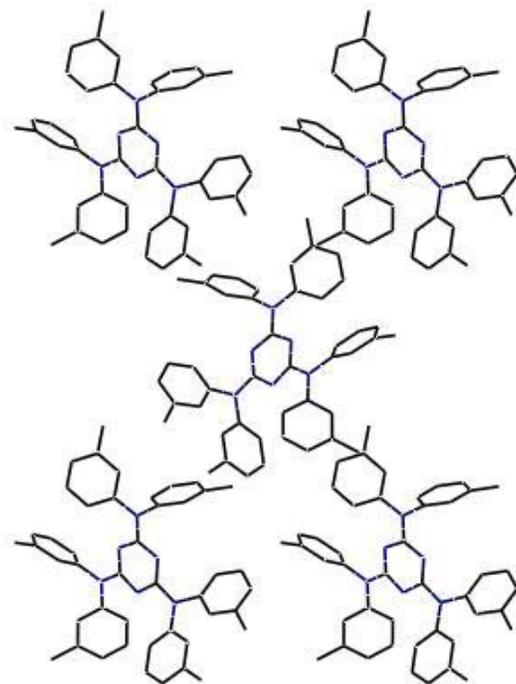
Figure 29. MDMETZ view down [001].

2. 2,4,6-(*p,p'*-ditolylamino)-1,3,5-triazine (PDMETZ)

PDMETZ molecule has the formula $C_{45}H_{42}N_6$ and formula weight of 666.85. It also

belongs to centrosymmetric space group $P2_1/c$. Relevant crystallographic data is given in

Table 3. Crystals were obtained from DMF in the form of tiny needles. As it can be seen

from Figure 30, this molecule also does not retain the trigonal symmetry in the crystalline

form. Here again the phenyl rings are not in the same plane as the central ring. Dihedral

angles between the planes belonging to phenyl rings attached to same nitrogen atom are

given in Table 6, and dihedral angles between the phenyl rings and central ring are given

in Table 7. Ring 3 is unusually bent unlike other rings, presumably because of the

interactions it is making; C-H..N and C-H..π bondings in [001] direction.

Table 6. PDMETZ dihedral angles between phenyl rings.

Cg	Cg	Alpha (^{o})
3	2	72.03
4	5	73.17
7	6	80.26

Table 7. PDMETZ dihedral angles between phenyl rings and central ring.

Cg	Cg	Alpha (^{o})
2	1	54.48
3	1	75.83
4	1	47.17
5	1	69.20
6	1	55.44
7	1	47.70

Offset stacked layers of molecules can be seen in Figure 31. The centroid to centroid distance of central rings between nearest molecules in adjacent layers is 6.921 Å; the angle between the planes of these central rings is 14° indicating that the layers are nearly flat. These nearest neighbors are connected to each other through three C-H...N bonds; each molecule donates two bonds and accepts one along [001]. These two molecules are translationally stacked along [001] and produce a columnar structure. Figures 32 and 33 show the packing of molecules along two other crystallographic axes. A view down 001 (Figure 34) shows the molecules along the column are in a zigzag arrangement. Figures 35 and 36 display the C-H…N and C-H…π contacts in the crystal structure.

Figure 30. PDMETZ molecule.

Figure 31. PDMETZ crystal view down [100].

Figure 32. PDMETZ crystal view down [010].

Figure 33. PDMETZ crystal view down [001].
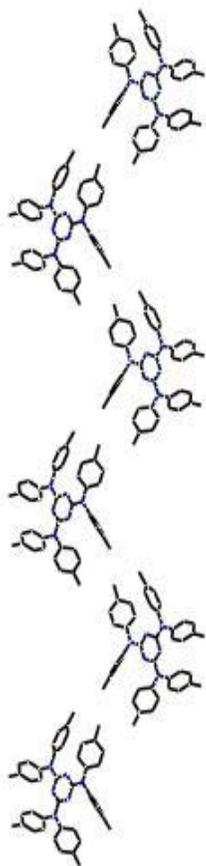
Figure 34. PDMETZ view down [001].

[010]

[001]
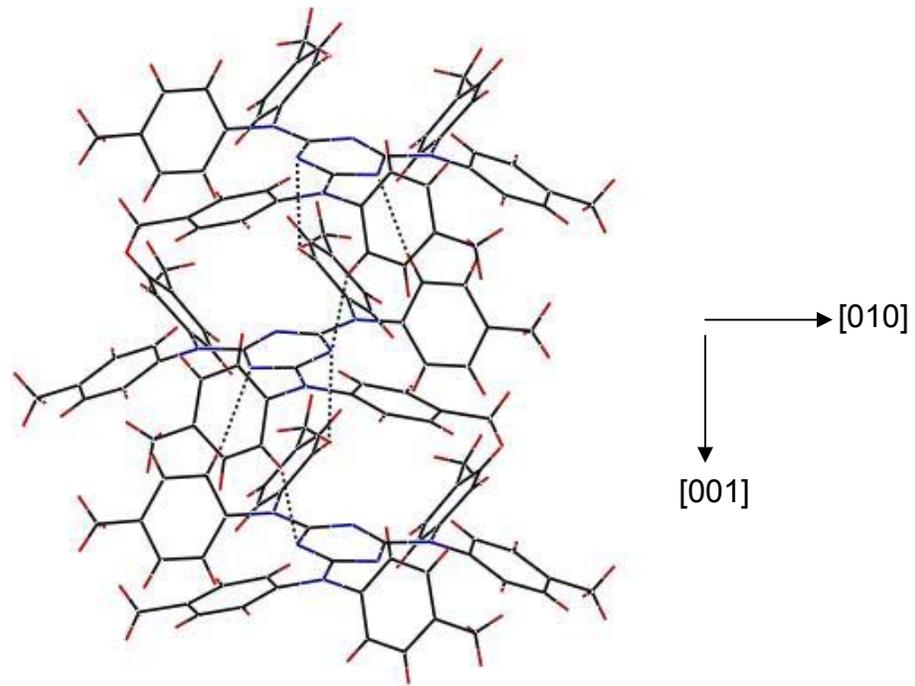
Figure 35. PDMETZ C-H..N bonds view down [100].

[010]

[001]
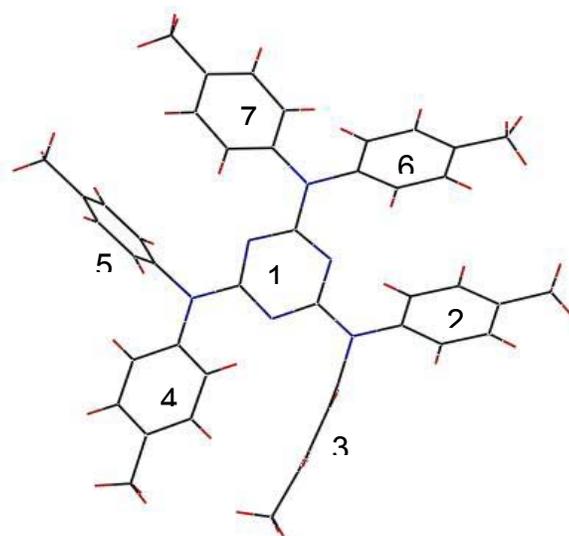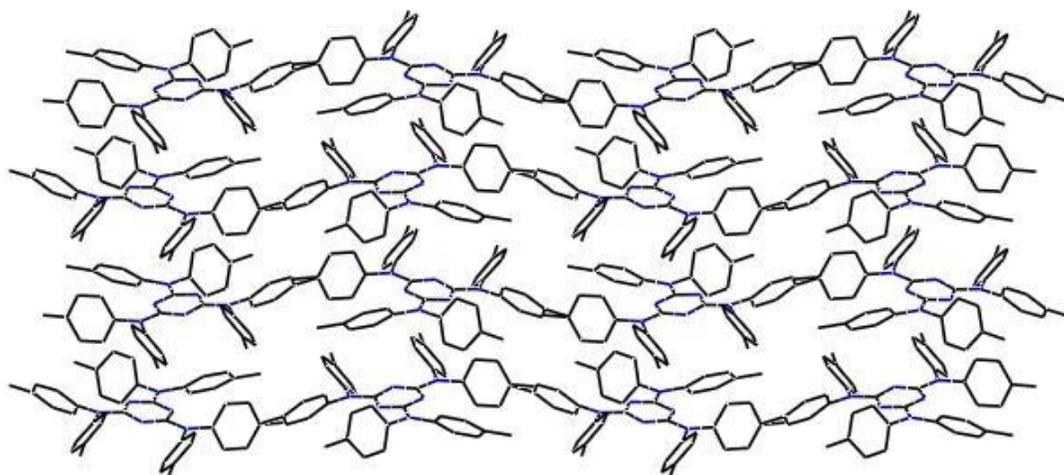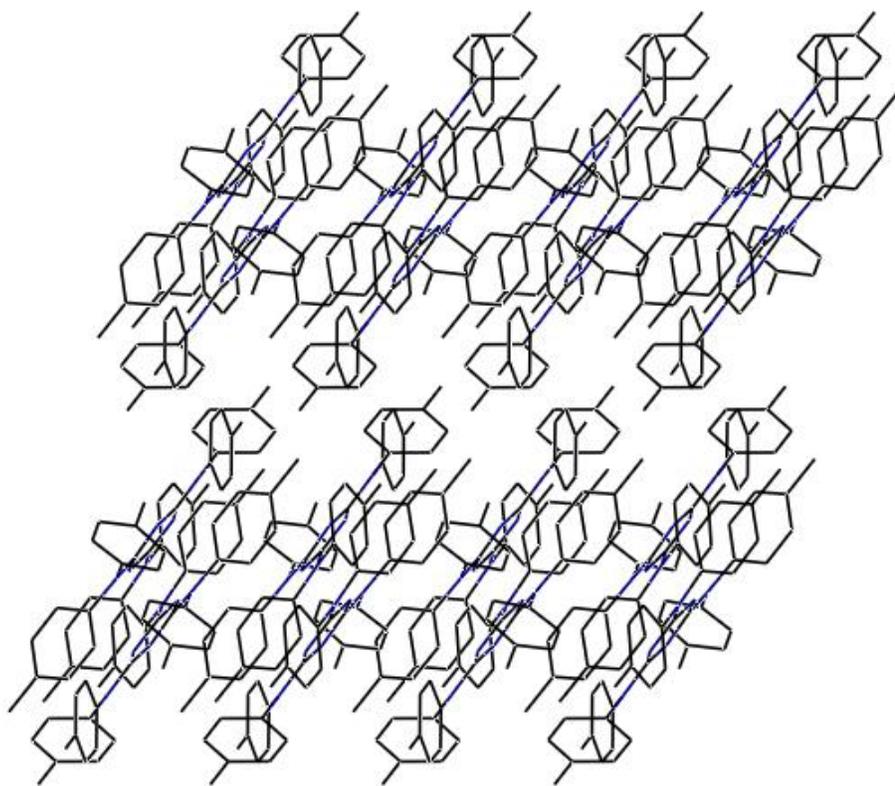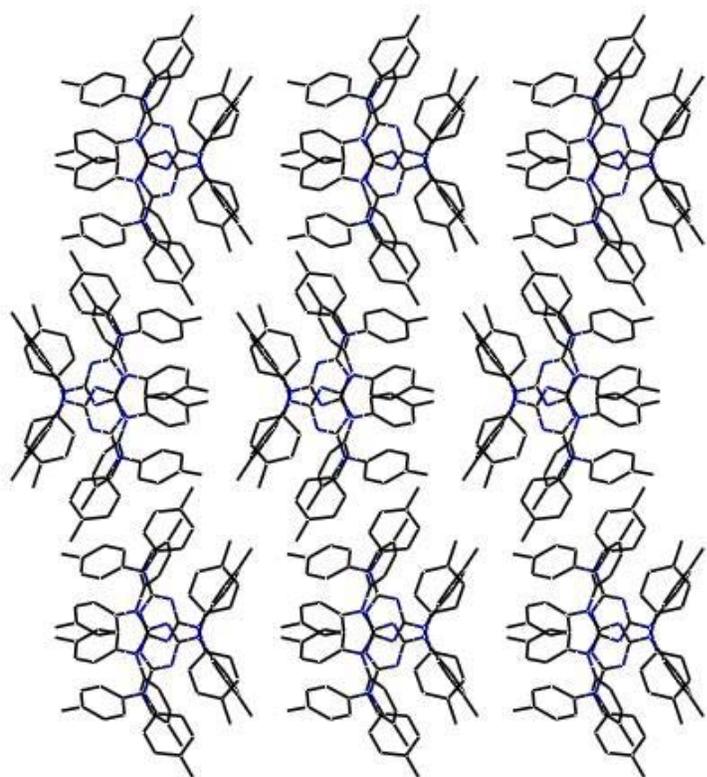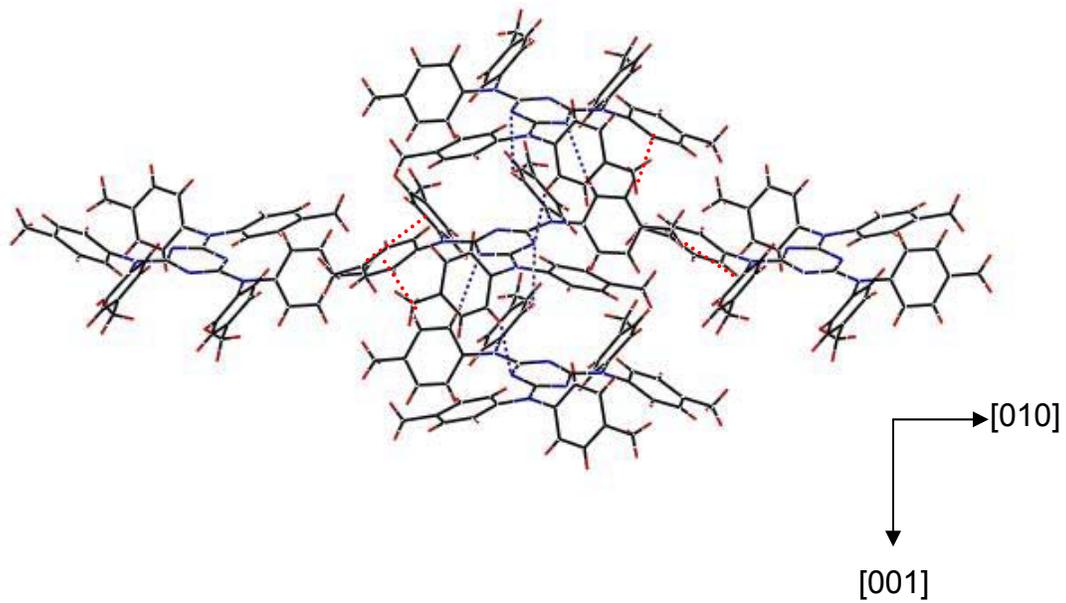
Figure 36. PDMETZ all interactions view down [100]
(C-H..N: blue; C-H..Cg: red).

3. 2,4,6-tris-(*p*-methyldiphenylamino)-1,3,5-triazine (PMETZ)

PMETZ molecule has the formula $C_{42}H_{36}N_6$ and formula weight of 666.85. it crystallizes in the centrosymmetric space group $P2_1/c$. The crystal is obtained from methanol in the form of tiny needles. Relevant crystallographic data is given in Table 3. This crystal structure is not completely solved yet. According to the data we obtained, molecule does not carry over the trigonal symmetry to the crystal (Figure 37). Instead of altering phenyl rings (one tolyl one benzyl), two tolyl rings are next to each other (numbered as 3 and 4 in Figure 37). The phenyl rings are not perpendicular to the central ring. Dihedral angles between the planes belonging to phenyl rings attached to same nitrogen atom are given in Table 8, and also dihedral plane angles between the phenyl rings and central ring are given in Table 9.

Table 8. PMETZ dihedral angles between phenyl rings.

Cg	Cg	Alpha (^{o})
3	2	83.32
4	5	80.99
7	6	85.36

Table 9. PMETZ dihedral angles between phenyl rings and central ring.

Cg	Cg	Alpha (^{o})
2	1	41.54
3	1	64.83
4	1	63.71
5	1	60.47
6	1	60.68
7	1	67.69

The crystal structure of PMETZ is very similar to PDMETZ. Figures 38, 39, and 40 show the molecular packing along three crystallographic axes. The view down [001] (Figure 40), illustrates that two molecules are on top of each other as in PDMETZ. These molecules are making an angle of 16.84° between the planes of central rings. They have 6.064 Å of centroid to centroid distance belonging to central rings. Figure 41 illustrates that molecules are in a zigzag arrangement in the column as seen in PDMETZ.

In Figure 38, molecules on top of each other are connected by C-H..N and C-H..π interactions: along [001] it is accepting two C-H..N bonding; and in the reverse direction it is donating two C-H..N and also donating one C-H..π (Figure 42). Through these bonds, molecules are assembling a columnar structure as in PDMETZ.

Figure 37. PMETZ molecule.

Figure 38. PMETZ crystal view down [100].

Figure 39. PMETZ crystal view down [010].
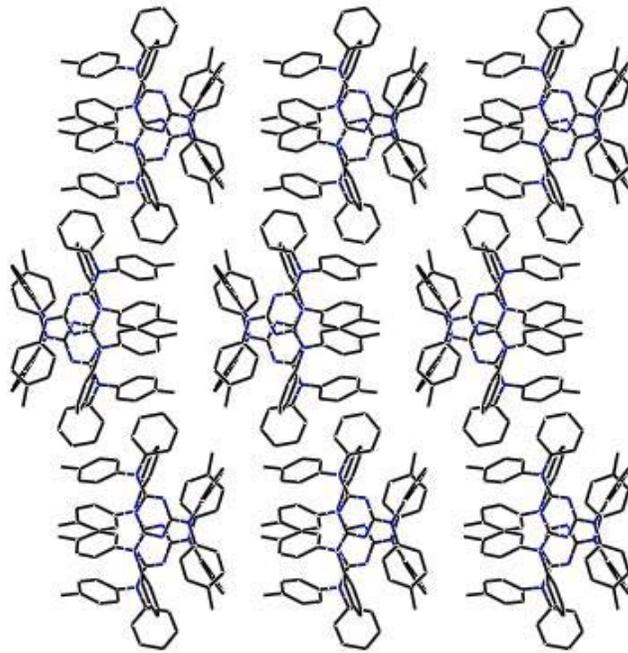
Figure 40. PMETZ crystal view down [001].

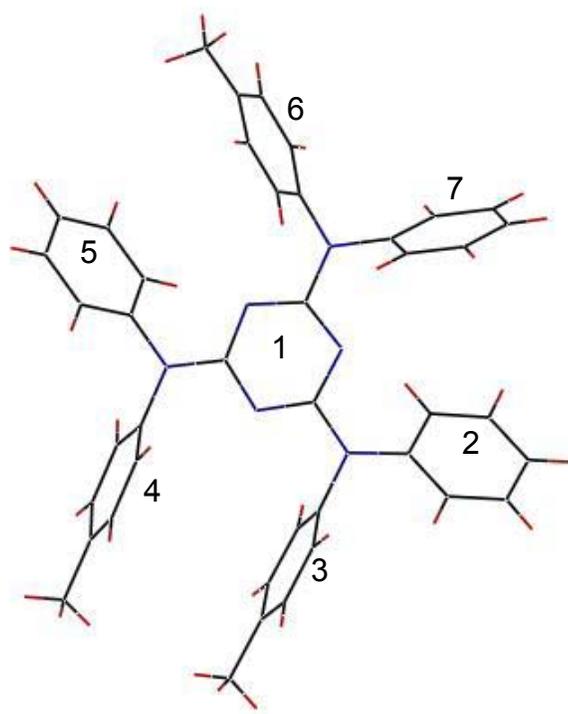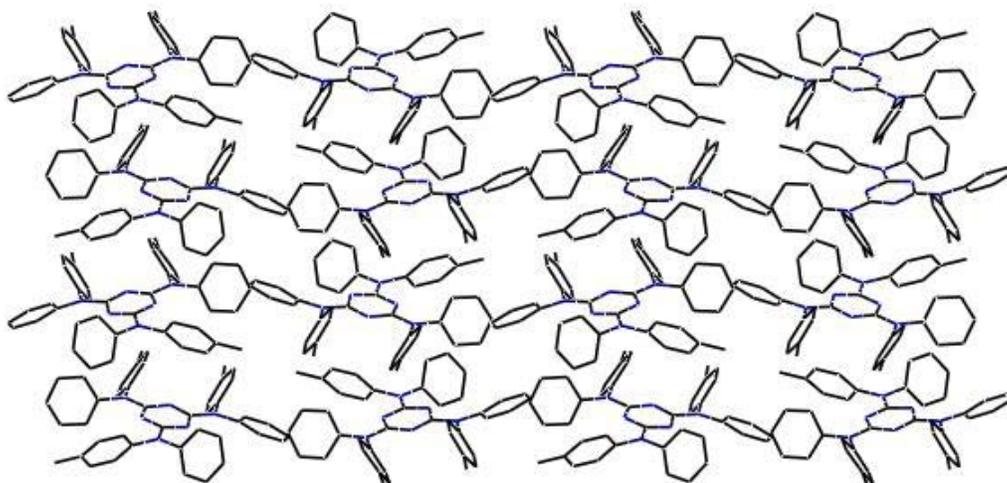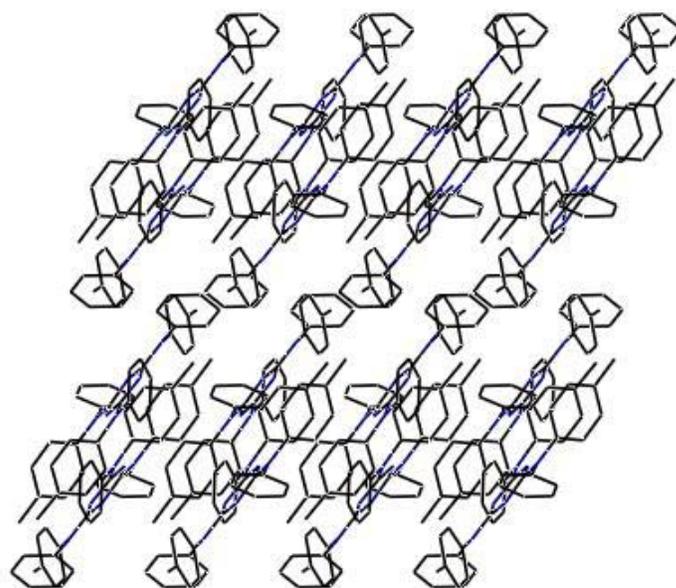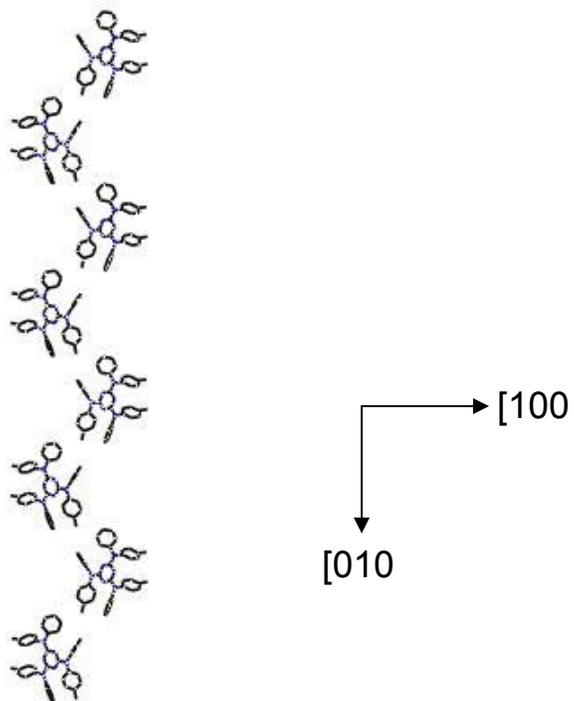Figure 41. Zig-zag shape formed by PMETZ molecules view down [001].
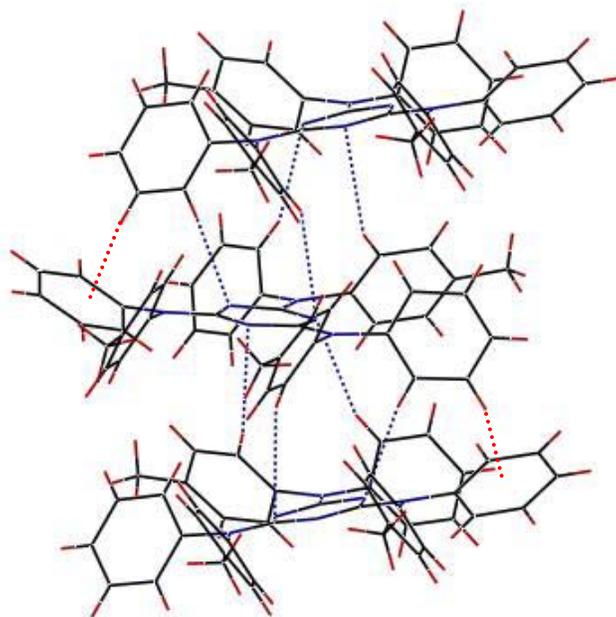
Figure 42. PMETZ all interactions
(C-H..N: blue; C-H..Cg: red).

Experimental Section

1. General Procedure for the Synthesis of Substituted Diphenylamines

In a pressure tube with stir bar, bromobenzene (8 mmol) and amine (4 mmol) were dissolved in 20 ml Toluene. After the addition of KOt-Bu (8 mmol), purged with Nitrogen and then the pressure tube was sealed and heated to 135 ^{o}C in an oil bath. After 36 hours, the reaction mixture was allowed to cool to room temperature and was quenched with 20 ml of water. The aqueous phase was extracted three times with 20 ml dichloromethane. The combined organic phases were dried over magnesium sulfate, and the solvent was removed in vacuo. The resulting crude product was purified by column chromatography.

p-methyldiphenylamine. Bromobenzene (1.2562 g, 8 mmol), aniline (0.36 ml, 4 mmol) and KOt-Bu (0.8977g, 8mmol) were reacted according to the general procedure. After column chromatography (Hexane: Ethyl acetate= 19:1) product was isolated as solid in 10% yield. Characterized by ^{1}H NMR and ^{13}C NMR.

2. General Procedure for the Synthesis of *tris*-(substituted diphenylamino)-triazines

Commercially available cyanuric chloride and the appropriate amines were used as received without further purification. Cyanuric chloride (4 mmol) and appropriate amine (12 mmol) were dissolved in 10 ml benzene and stirred for 2 hours. The benzene was distilled as the sand bath temperature was raised to 200+ ^{o}C. Hydrogen Chloride was smoothly evolved in this temperature range and the reaction was complete in 1.5 hours.

2,4,6-(*m,m'*-ditolylamino)-1,3,5-triazine (MDMETZ). Cyanuric chloride (0.922 g, 5 mmol) and *m,m'*-ditolylamine (2.959 g, 15 mmol) were reacted according to the general procedure. The flask containing the reactants was gradually heated to 290 $^{\circ}$C in a sand bath. Once the temperature is stabilized, the flask was gradually cooled down to room temperature and the crude reaction product was extracted with boiling ethanol leaving a residue of crude MDMETZ. The product was characterized by ^{1}H NMR (Figure 43.) and ^{13}C NMR (Figure 44.) spectroscopy.

2,4,6-(*p,p'*-ditolylamino)-1,3,5-triazine (PDMETZ). Cyanuric chloride (0.3116 g, 1.69 mmol) and *p,p'*-ditolylamine (1.000 g, 5.07 mmol) were reacted according to the general procedure. Temperature raised to 310 $^{\circ}$C. Cooled down to room temperature and crude reaction product was extracted with boiling ethanol leaving a residue of crude PDMETZ. Characterized by ^{1}H NMR (Figure 45.) and ^{13}C NMR (Figure 46.).

2,4,6-tris-(*p*-methyldiphenylamino)-1,3,5-triazine (PMETZ). Cyanuric chloride (0.168 g, 0.913 mmol) and *p*-methyldiphenylamine (0.500 g, 2.73mmol) were reacted according to the general procedure. Temperature raised to 220 $^{\circ}$C. Cooled down to room temperature and crude reaction product was extracted with methanol. Characterization was done by ^{1}H NMR (Figure 47.) and ^{13}C NMR (Figure 48.).

2,4,6-tris-(*m*-methyldiphenylamino)-1,3,5-triazine. Cyanuric chloride (1.844 g, 10 mmol) and 3-methyldiphenylamine (5.157 ml, 30 mmol) were dissolved in toluene and refluxed for 2 hours. Distilled toluene and then raised the temperature to 200 $^{\circ}$C

in 1.5 hours. Cooled to room temperature and the product washed with methanol. Characterization was done by ^{1}H NMR (Figure 49.) and ^{13}C NMR (Figure 50).

2,4,6-tris-(*p*-hydroxydiphenylamino)-1,3,5-triazine. Cyanuric chloride (1.106 g, 6 mmol) and 4-hydroxydiphenylamine (3.33 g, 18 mmol) and potassium carbonate (1.244 g, 9 mmol) were mixed in 50 ml toluene. Refluxed for 48 hours. Solid washed with 200 ml hot water and then 50 ml toluene. Characterized by ^{1}H NMR (Figure 51.) and ^{13}C NMR (Figure 52.).

2,4,6-tris-(*m*-methoxydiphenylamino)-1,3,5-triazine. Cyanuric chloride (1.844 g, 10 mmol) and 3-methoxydiphenylamine (5.977 g, 30 mmol) were dissolved in 50 ml toluene. Refluxed for 2 hours under nitrogen. Toluene distilled and the temperature raised to 220 $^{\circ}$C over 1.5 hours. Cooled to room temperature and washed with methanol. Characterization done by ^{1}H NMR (Figure 53.) and ^{13}C NMR (Figure 54.).

2,4,6-tris-(*N*-phenyl-1-naphthylamino)-1,3,5-triazine; 2,4,6-tris-(*N*-phenyl-2-naphthylamino)-1,3,5-triazine; 2,4,6-tris-(*p*-nitrosodiphenylamino)-1,3,5-triazine; 2,4,6-tris-(*p*-nitrodiphenylamino)-1,3,5-triazine and 2,4,6-tris-(*m*-hydroxydiphenylamino)-1,3,5-triazine. The synthesis of these compounds was attempted according to the general procedure; most reactions yielded several byproducts; these products currently being purified. Also we tried to convert the methyl groups of PDMETZ and MDMETZ to COOH groups by $KMnO_4$ and organic equivalent of $KMnO_4$ (^{n}Bu$_4$NMnO$_4$); these reactions have not been successful.

Summary and Conclusion

Here we showed the synthesis of diarylamines exhibiting different functional groups on two phenyl rings. The successful attempt was in the case of phenyl-*p*-tolylamine, but we believe that different diarylamines can be synthesized by this procedure without any need of complex reaction conditions. We synthesized 2,4,6-arylamino-1,3,5-triazines both for the purpose of as a new family, and as intermediates for further synthesis of targeted triazines. We showed the successful coupling of diarylamines with cyanuric chloride to obtain the targeted molecules of 2,4,6-diarylamino-1,3,5-triazines. We successfully obtained the crystals of the products 2,4,6-(*m,m'*-ditolylamino)-1,3,5-triazine, 2,4,6-(*p,p'*-ditolylamino)-1,3,5-triazine and 2,4,6-(phenyl-*p*-tolylamino)-1,3,5-triazine. By successful retrosynthetic analysis we arrived at the targeted triazines, and showed that triazines synthesized may be accepted as molecular analogs of ideal Piedfort units formed by cofacial dimers of 2,4,6-arylamino-1,3,5-triazine molecules as formed in the previous case of 2,4,6-triaryloxy-1,3,5-triazines. All the crystals obtained exhibit methyl substituents, so far they belong to centrosymmetric space group $P2_1/c$. Though none of the molecules retain trigonal symmetry in the crystal structures, pseudo-trigonal assembly of molecules is identified in some cases. The assembly of molecules within the crystals results in columnar structures formed by C-H..N and C-H..π interactions. We believe that some other functional groups other than methyl group may give us targeted two-dimensional noncentrosymmetric networks.
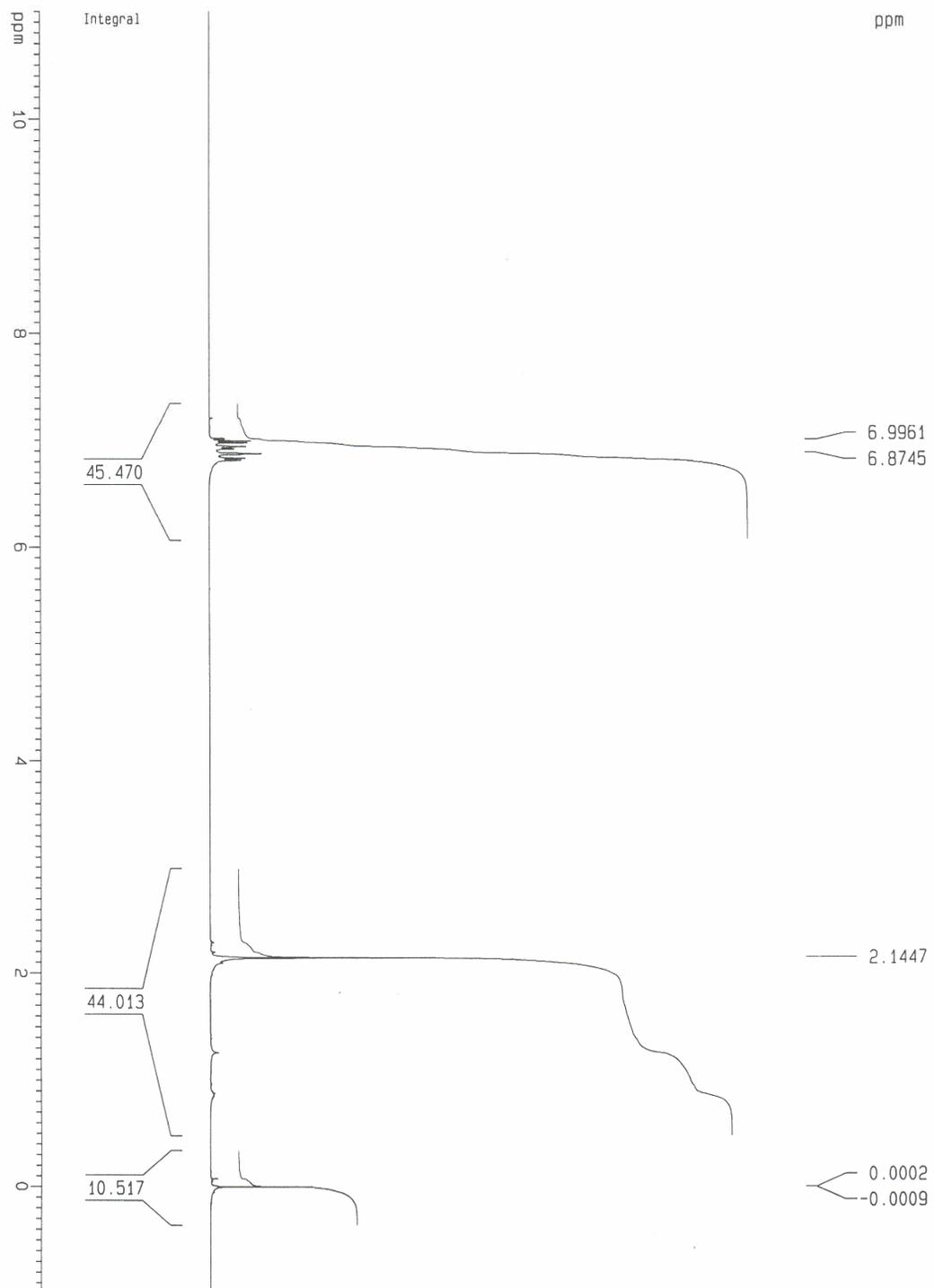
Figure 43. Spectrum 1. MDMETZ ^{1}H
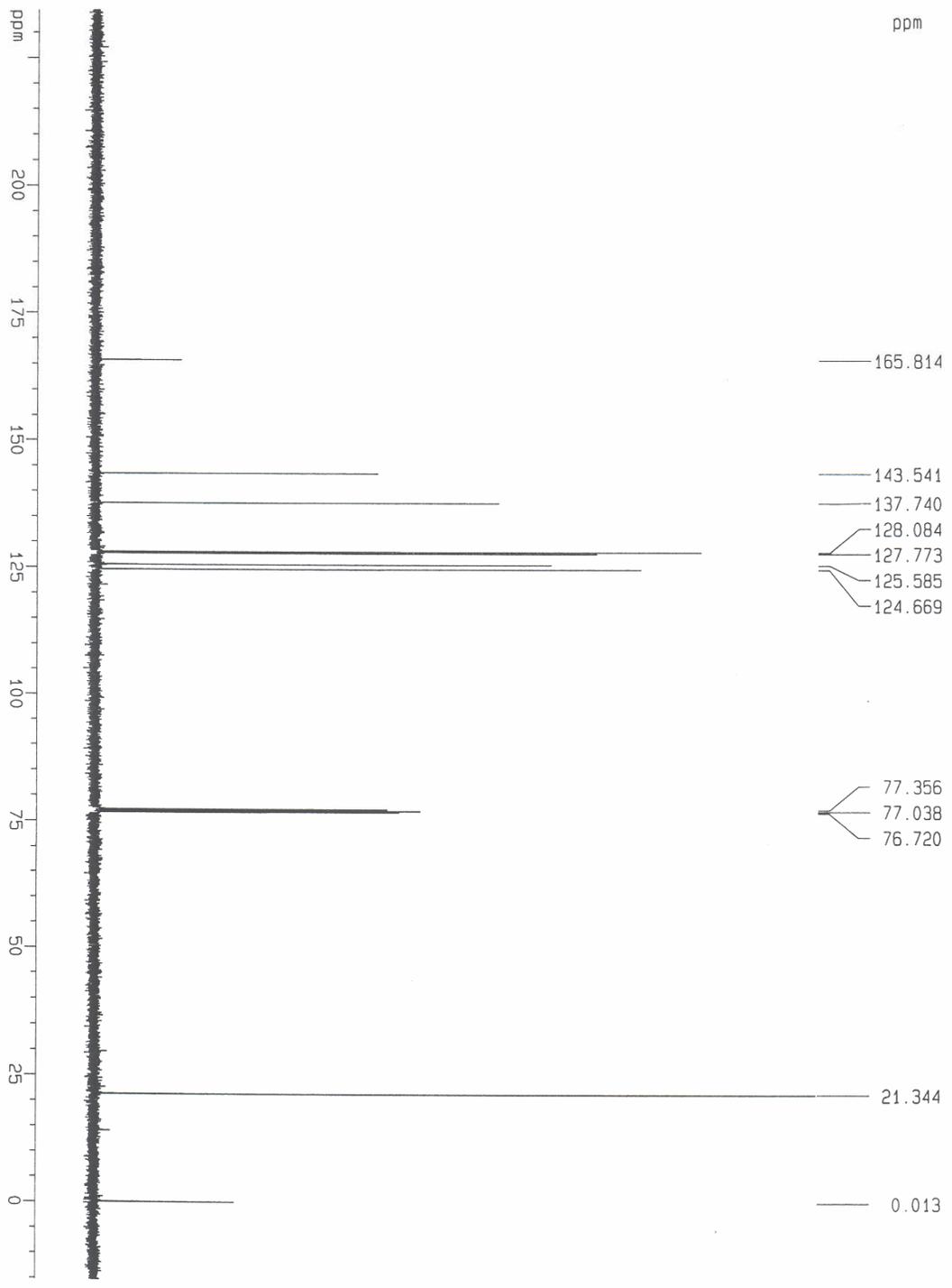
Figure 44. Spectrum 2. MDMETZ ^{13}C

ppm

165.814

143.541
137.740
128.084
127.773
125.585
124.669

77.356
77.038
76.720

21.344

0.013

Figure 45. Spectrum 3. PDMETZ ^{1}H

Integral

ppm

45.049

8.1071
7.6969
7.5415
7.5326
7.5274
7.2550
7.2025
7.1801
7.1138
7.1055
7.0868
7.0531
7.0327
7.0021
6.9815
6.9504
6.9163
6.8957
6.7210
6.7022

0.371

4.2333
4.2188
4.2031

44.504

2.3281
2.3030
2.2767
2.2253
2.1175
1.5361
1.4847
1.3474
1.3183
1.3061
1.2814
1.2533

10.076

0.9386
0.9201
0.9012
0.8954
0.8864
0.0702
0.0522
0.0000
-0.0516
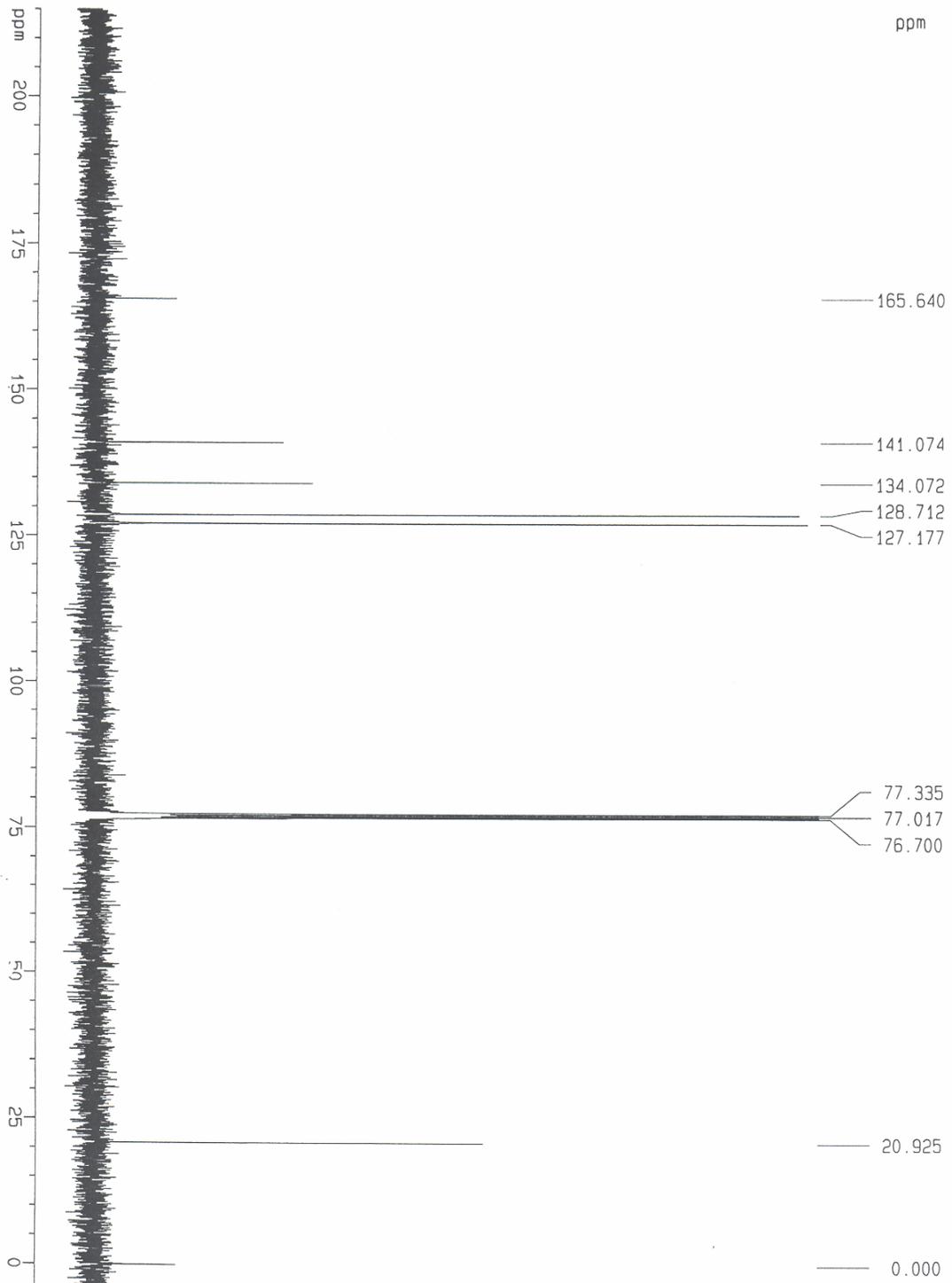
Figure 46. Spectrum 4. PDMETZ ^{13}C

ppm

165.640

141.074
134.072
128.712
127.177

77.335
77.017
76.700

20.925

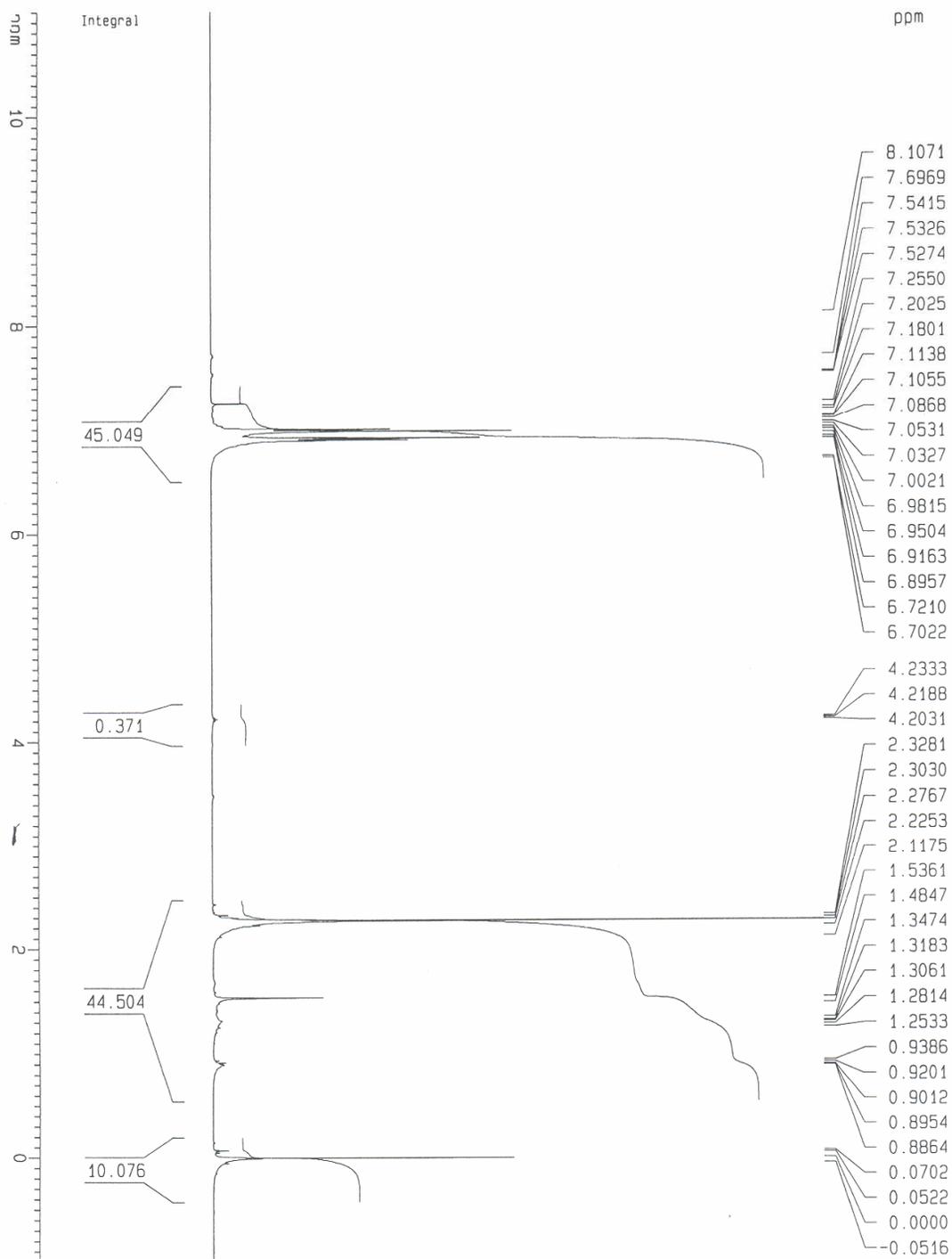0.000

62
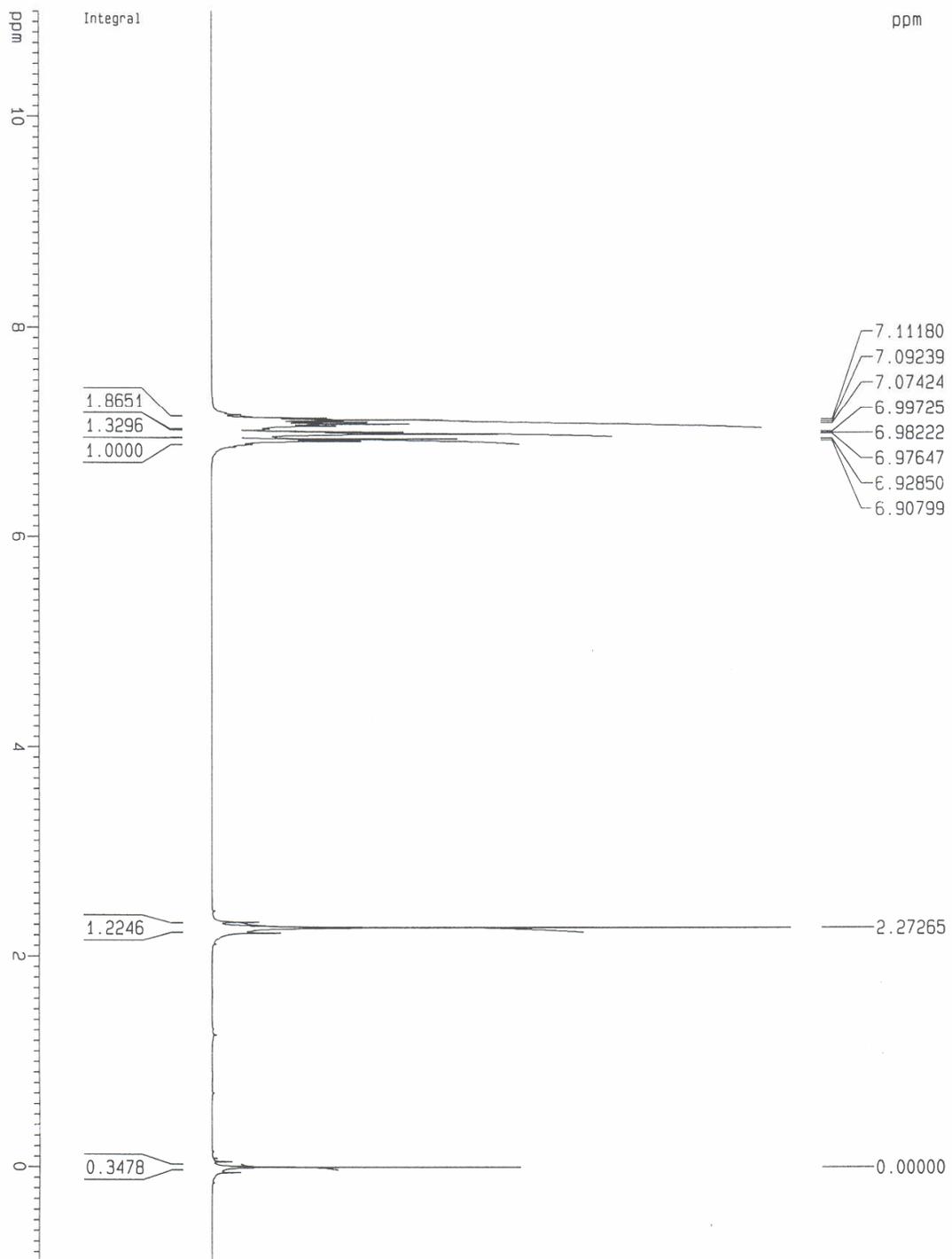
Figure 47. Spectrum 5. PMETZ ^{1}H
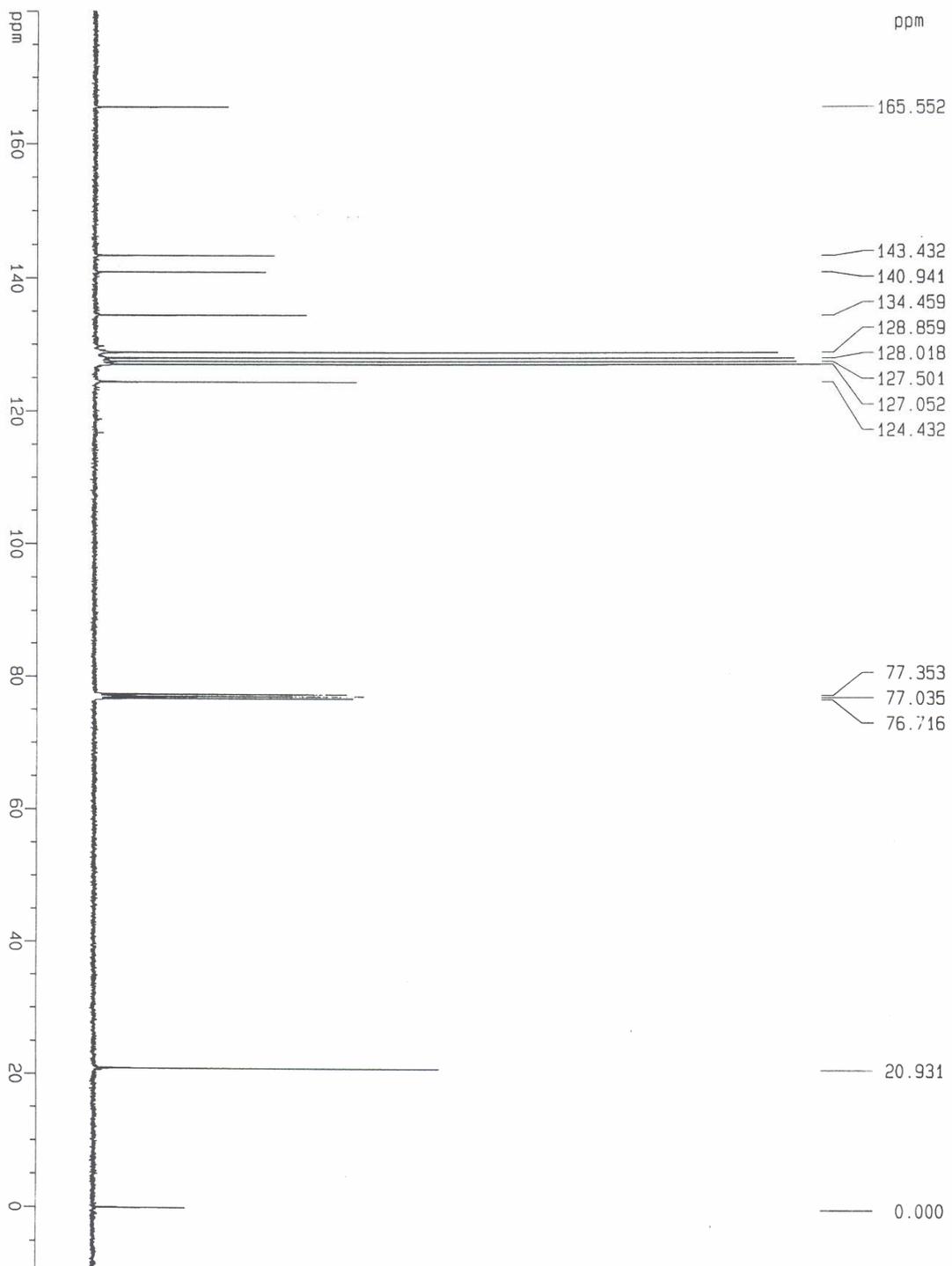
Figure 48. Spectrum 6. PMETZ ^{13}C
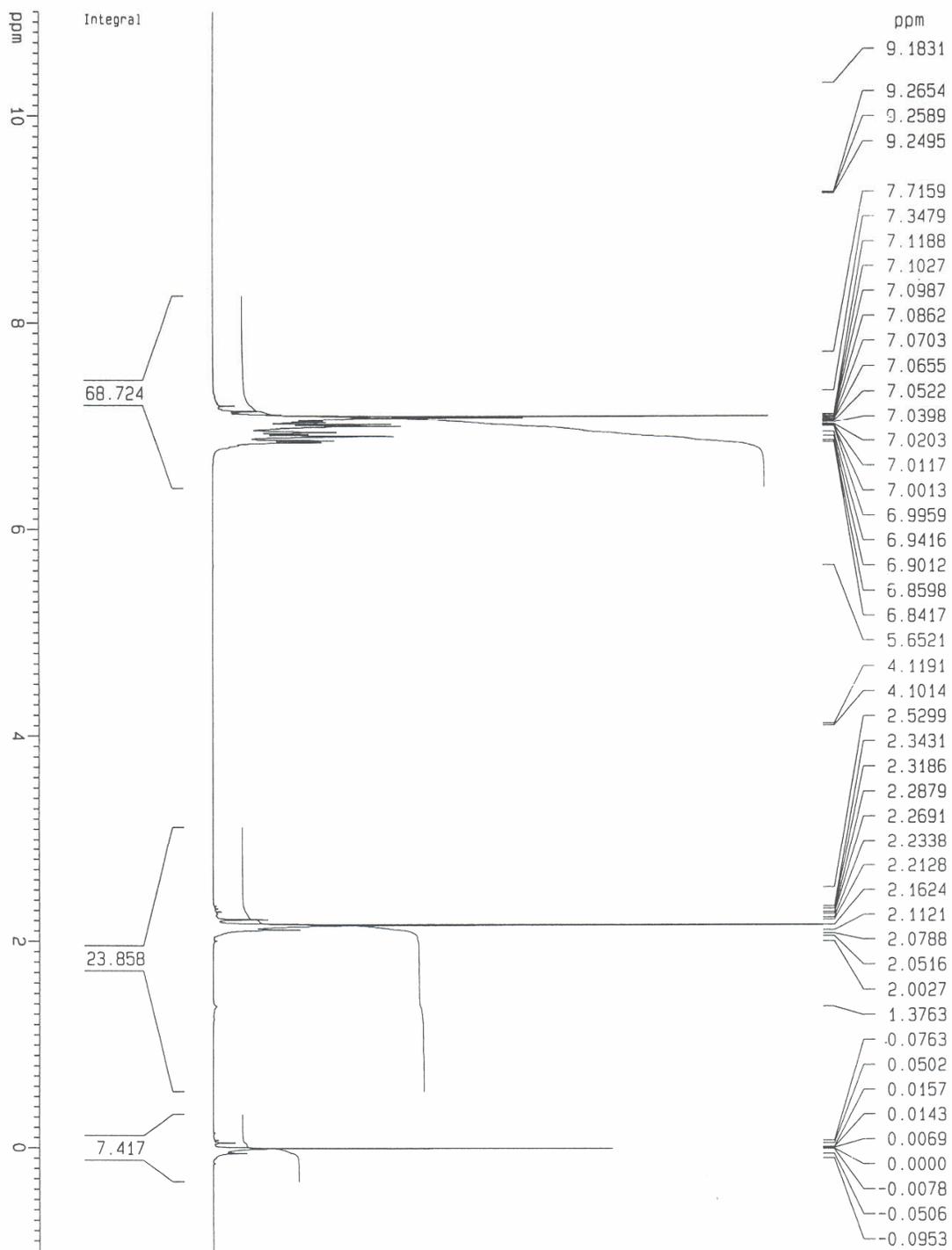
Figure 49. Spectrum 7. MMETZ ^{1}H
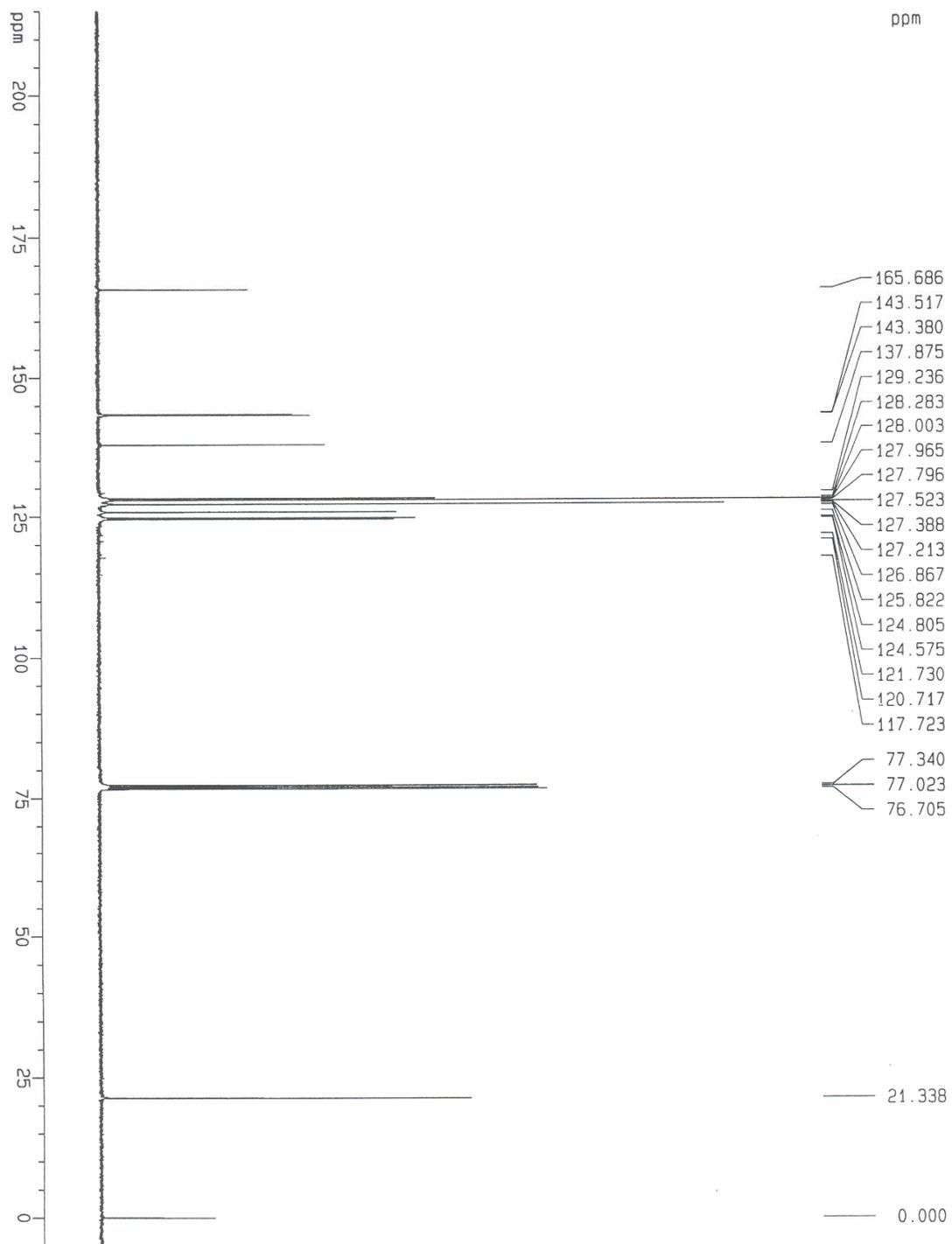
Figure 50. Spectrum 8. MMETZ ^{13}C

ppm

200

175

150

125

100

75

50

25

0

ppm

165.686
143.517
143.380
137.875
129.236
128.283
128.003
127.965
127.796
127.523
127.388
127.213
126.867
125.822
124.805
124.575
121.730
120.717
117.723

77.340
77.023
76.705

21.338

0.000

Figure 51. Spectrum 9. POHTZ ^{1}H

ppm
9.1165
9.0767
9.0424
9.0189
8.9485
8.9244
7.6012
7.3174
7.0143
6.9806
6.9639
6.9630
6.9515
6.9461
6.8786
6.8627
6.7950
6.7899
6.7783
6.7731
6.7651
6.5075
6.5022
6.4907
6.4855
4.8626
4.8117
4.7610
4.0117
3.9939
3.9761
3.9582
3.2100
3.2061
3.2022
3.1981
3.1942
1.8974
1.1766
1.1592
1.1423
1.1245
1.1067
0.7918
0.7859
0.7678
0.0000
-0.1000

Integral

68.818

11.609

2.011

2.766

14.797

Figure 52. Spectrum 10. POHTZ ^{13}C

ppm

200
175
150
125
100
75
50
25
0
ppm

173.416
167.489
156.557
145.650
137.319
130.666
129.588
128.565
125.965
116.552

61.965
50.066
49.853
49.640
49.427
49.214
49.001
48.788
31.222
21.303
14.895

68

Figure 53. Spectrum 11. MMOTZ ^{1}H

ppm
10.7459
10.3043
10.2502
8.1058
8.0834
7.7868
7.4006
7.1385
7.1220
7.1053
7.0846
7.0608
7.0406
7.0339
7.0285
7.0203
7.0126
6.7278
6.7083
6.6868
6.6814
6.6766
6.6259
6.6204
3.8004
3.7702
3.7610
3.6984
3.6681
3.6588
3.6543
3.6233
3.6006
3.5770
3.4414
2.1712
2.0393
1.5053
1.2536
1.2352
0.1460
0.0965
0.0878
0.0740
0.0475
0.0000
-0.0468
-0.1494

Integral
60.156
18.670
0.610
20.564

ppm
10
8
6
4
2
0

69

Figure 54. Spectrum 12. MMOTZ ^{13}C

REFERENCES
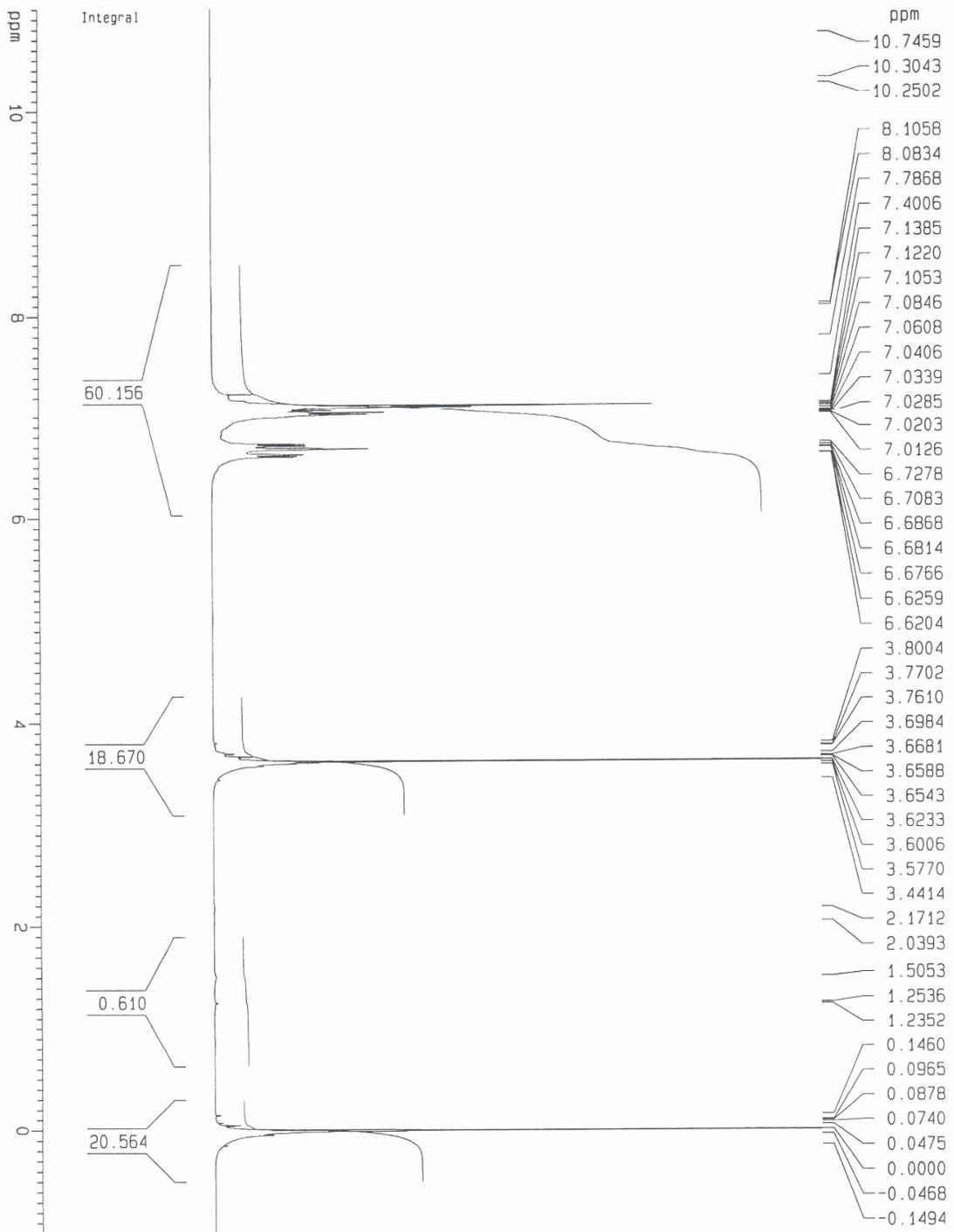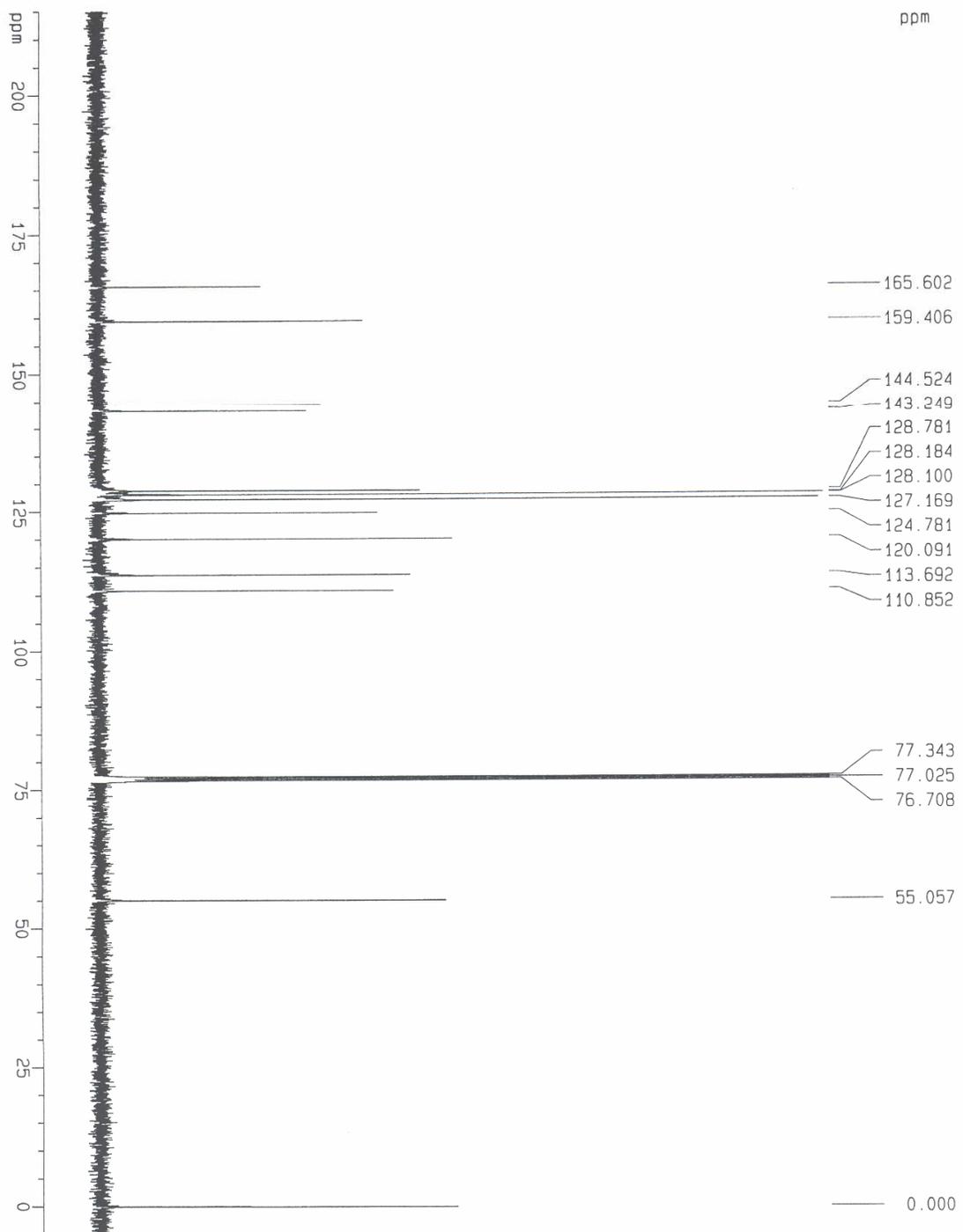
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