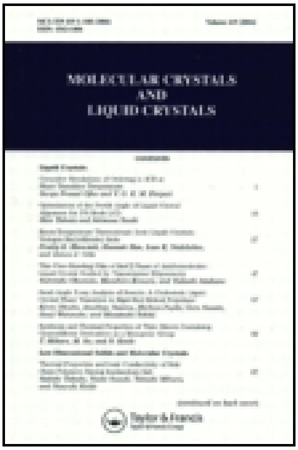


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Design and Synthesis of New Octupolar Molecules for Second-Harmonic Generation

Olivier Riant [a], Guillaume Bluet [a], Sophie Brasselet [b], Nadine Druze [a], Isabelle Ledoux [b], Fabrice Lefloch [a], Alexandre Skibniewski [a] & Joseph Zyss [a]

[a] Laboratoire des Réactions Organiques Sélectives (URA CNRS 1497), ICMO, Bt 420, Université Paris-Sud, 91405, Orsay cedex, France

[b] Laboratoire d'Electronique Quantique et Moléculaire (UA CNRS 250), CNET, 196 Av. Henri Ravera, 92225, Bagneux Cedex, France

Version of record first published: 24 Sep 2006

To cite this article: Olivier Riant, Guillaume Bluet, Sophie Brasselet, Nadine Druze, Isabelle Ledoux, Fabrice Lefloch, Alexandre Skibniewski & Joseph Zyss (1998): Design and Synthesis of New Octupolar Molecules for Second-Harmonic Generation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 322:1, 35-42

To link to this article: http://dx.doi.org/10.1080/10587259808030197

Mol. Cryst. Liq. Cryst., Vol. 322, pp. 35–42
Reprints available directly from the publisher
Photocopying permitted by license only

Design and Synthesis of New Octupolar Molecules For Second-Harmonic Generation

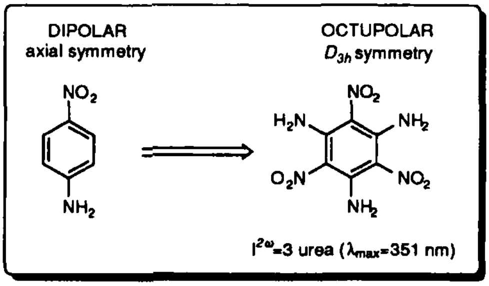
OLIVIER RIANT[a]*, GUILLAUME BLUET[a], SOPHIE BRASSELET[b], NADINE DRUZE[a], ISABELLE LEDOUX[b], FABRICE LEFLOCH[a], ALEXANDRE SKIBNIEWSKI[a], and JOSEPH ZYSS[a]
[a]Laboratoire des Réactions Organiques Sélectives (URA CNRS 1497), ICMO, Bt 420, Université Paris-Sud, 91405 Orsay cedex, France; [b]Laboratoire d'Electronique Quantique et Moléculaire (UA CNRS 250), CNET, 196 Av. Henri Ravera, 92225 Bagneux Cedex, France

Received 10 June 1998; accepted 14 June 1998

The state of the art concerning the design of octupoles, a new familly of NLO active molecules is presented here. 2D and 3D based architectures with higher symmetries lead to high efficiencies for SHG.

Keywords: Non Linear Optics, Second Harmonic Generation, Octupoles, organometallic complexes.

Organic materials for Non-Linear Optics have been intensively investigated during the past 20 years in view of numerous applications in the field of telecommunications[1,2]. However, studies have been mainly restricted to the design of organic and organometallic molecules displaying a one dimension dipole structure. Optimisation of the structural parameters such as the strength of the donor and acceptor group, lenght and nature of the spacer has led to high values for the quadratic hyperpolarisabilities β. Considerable efforts consequently been made to built new materials by inserting NLO active dipolar molecules in solid matrix in non-centro symmetric arrangements. Some drawbacks however arise from the dipolar nature of 1D chromophores such as poor solubility and strong absorption of the second harmonic by the chromophore, thus leading to reduced efficiency-transparency trade off. One possibility to get over this limitation is to increase the degree of symmetry of the molecule in order to improve the transparency of the molecule. It was indeed shown that a new family of 2D and 3D chromophores called *Octupoles* could fit the required properties for efficient SHG while displaying a non dipolar structure. The first example of such molecules, namely TATB, was described in 1990 by Lehn, Zyss *et al*[3] (Scheme 1).



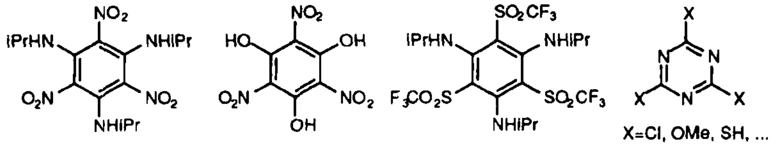
Scheme 1

As compared to PNA, a true dipolar molecule, TATB can be regarded as a superposition of three molecules of PNA, each showing a rotation of nx120° (n=0-2) leading to a D_{3h} overall symmetry. This prototype shows the requirement for a octupole which combines the *cancellation of vectorial properties* and *a non-centrosymmetric structure*. SHG for TATB was evaluated by powder measurement and it was later shown that the arrangement in the crystal was due to a non-centrosymmetric polymorph in the bulk[4].

At this point, one can wonder what advantages can be expected for octupolar architectures compared to pure dipolar ones. As it was already pointed out, working with higher-order symmetry should lead to improvement of nonlinearity/transparency trade-off[5], a crucial parameter to consider while designing NLO devices. It could be also expected that working with molecules displaying higher-order symmetry as well as a lack of dipole moment might lead to preferential non-centrosymmetric crystallisation, thus making octupolar molecules good candidates for crystal engineering of efficient NLO material[6]. On the other hand parametrisation of SGH properties was made difficult for octupoles as their lack of dipole moment precluded their studies by traditional methods such as EFISH. However, it was found that a method discovered in 1965 by Maker *et al.*[7], called hyper-Rayleigh scattering (HRS) could be used for measurement of hyperpolarisabilities β of molecules devoid of dipole moment such as octupoles[8] as well as for ionic molecules[9]. This method was proved to be very efficient for measurement of non linear efficiencies β, however it should be pointed out that great care should be taken when using it as spurious results were often encountered, leading to overestimation of β[10]. Those overestimation were due to parasitic phenomenon such as two-photon induced fluorescence and some β values have been recently restated[11].

Since the first publication on TATB in 1990, many octupoles with 2 and 3D structures have been prepared and their efficiencies measured. The theoretical aspect of multipoles has been already reviewed[12] and we whish here to focus on the state of the art concerning the design of octupolar molecules by a classification according to the structure and the nature of the octupole.

2D neutral octupoles



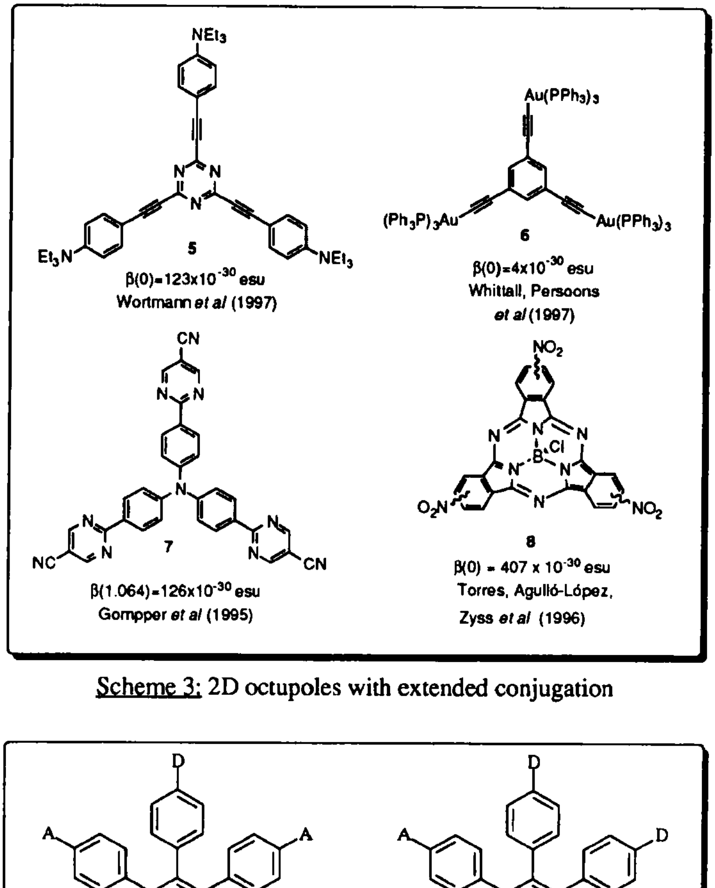
1 **2** **3** **4**

1,2 K. Clays *et al* (1994) 1,3 Wortmann *et al* (1997) 4 P.C. Ray and P.K. Das (1995)

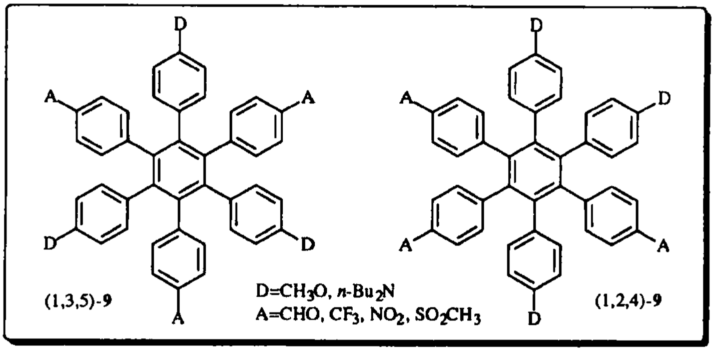
Scheme 2: first generation of 2D octupoles

Various D_{3h} hexasubstituted benzenes such as **1-3** and trisubstituted triazines **4** have been prepared[13], after the prototype TATB and in some cases their efficiency was compared to the dipole analogue. A careful measurement of β was performed on **1** and **4** by Wortmann *et al*[13c], showing an equivalent order of magnitude for the values obtained for **1** ($\beta(0)=8.1\times10^{-30}$ esu measured at $\lambda=1064$ nm) and *p*-nitroaniline PNA ($\beta(0)=13.5\times10^{-30}$ esu). When the nitro group was replaced by the stronger CF_3SO_2 group, a decrease of the $\beta(0)=4.8\times10^{-30}$ esu was observed. The decrease in the values observed for **1** and **2** compared to PNA could be explained by the strong steric hindrance on the benzene ring, leading to decrease of the overall conjugation due to non planar conformations.

Extended D_{3h} planar structures have also been prepared in view of optimisation of NLO efficiencies[13c,14-16] (Scheme 3). In chromophores such as **5**[13c] and **7**[14], a donor (amino) or acceptor (triazine) core is connected by three conjugated bridges to three acceptor (cyano) or donor (amino) groups. As this situation favours planar comformation and therefore improved electronic communication between the different groups, increased efficiencies were measured by HRS. An organometallic octupole **6**[15] in which three metal atoms are connected to a central benzene ring has been described. A high β(0) value was also reported for a boron subphtalocyanine **8**[16]. In this later case, measurement of the efficiency was performed on a mixture of C_1/C_3 isomers.



Scheme 3: 2D octupoles with extended conjugation

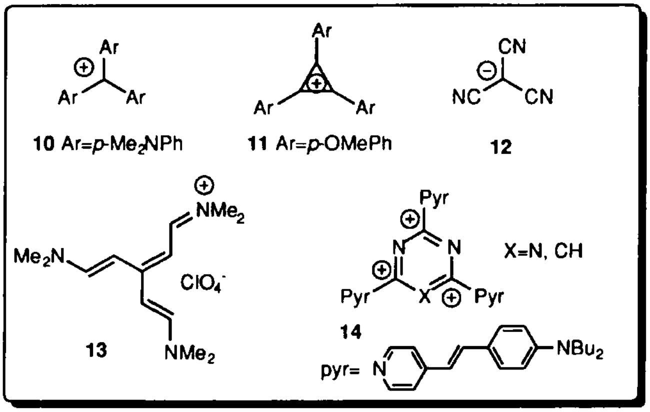


Scheme 4

We have been interested into the design of new octupoles based on a hexaarylbenzene architecture[17]. Transition metal catalysed [2+2+2] cyclotrimerisation of donor-acceptors bis-aryl acetylenes gave a straightforward access to both isomers of **9** (Scheme 4) in which various donor and acceptor groups can be introduced. Single crystal RX analysis on (1,3,5)-**9** (D=OMe, A=CF$_3$) showed a non planar helicoidal structure with a D_3 chiral symmetry.

HRS measurement gave a $\beta(0)=18\times10^{-30}$ esu and a $\beta_{J=3}/\beta_{J=1}=5.5$, proving thus that this molecule behaves as a true octupole.

2D ionic octupoles

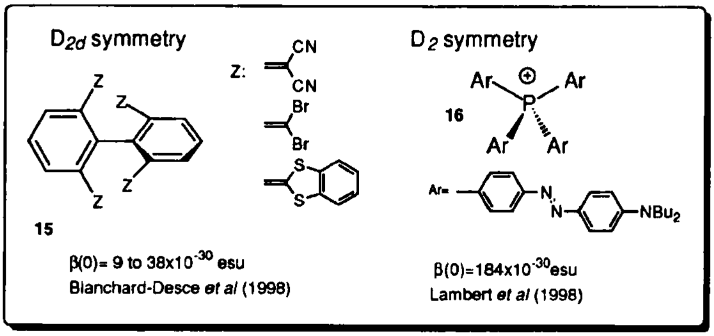


Scheme 5: 2D ionic octupoles

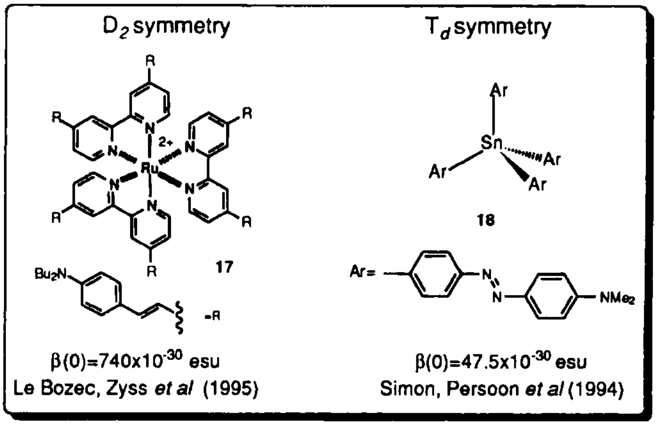
As it is already well known for dipolar molecules, the introduction of a cationic centre in a chromophore can lead to high NLO efficiencies due to its strong electron-withdrawing character (Scheme 5). Application to the case of octupolar molecules have been early reported for violet crystal **10**[13a,18] and the cyclopropenylium cation **11**[13a]. C_{3h} symmetric cyanine **13**[13c] displayed a $\beta(0)=30\times10^{-30}$ esu and it was shown that values of hyperpolarisabilities increased with increasing conjugation length. The only anionic octupole described so far is the tricyanimethanide **12** and has been independently reported by two groups[19]. We also also prepared some tricationic octupoles **14**[17] in which three stilbenyl pyridinium groups are linked to a central electron deficient aromatic core.

3D octupoles

The design of 3D octupoles with higher symmetry is a fascinating challenge for synthetic chemists. Tetrahedral architectures have been chosen by different groups for the construction of such molecules (Scheme 6). Banchard-Desce *et al*[20] have recently described some tetrasubstituted biphenylene chromophores with D_{2d} symmetry **15** in which ortho substitution by donor or acceptor groups brings the two phenylene moieties in an orthogonal conformation. NLO efficiencies increase for a strong donor substituent but the main advantage of such molecules is that they display high transparency. Another elegant tetrahedral octupole was reported by Lambert *et al*[21] for the tetraarylphosphonium cation **16**. PM3 geometry optimisation gave a D_2 symmetry for this chromophore and an excellent value for the hyperpolarisability was measured by HRS.

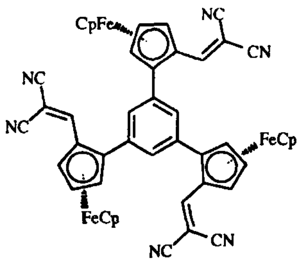


Scheme 6: 3D tetrahedral octupoles



Scheme 7: 3D organometallic octupoles

Two organometallic octupoles for which a 3D structure has been built around a ruthenium or a tin atom have been reported (Scheme 7). In the case of ruthenium complex **17**[22], each bipyridine ligand is substituted by two aminostyryl pendants thus leading to an extended conjugated structure and a strong metal to ligand charge transfer. The arrangement of the three ligands around the central metal atom gives a chiral D_3 symmetry for this original molecule. In the second case, introduction of four aminosubstituted phenylazo groups around the central tin atom gave the tetrahedral octupole **18**[23] with T_d symmetry. Comparison of the β measured for **18** with the 1D dipolar analog gave a comparable value.



β(1.34 nm)=105x10^{-30}esu
λ_{max}=530 nm
β(0)=33x10^{-30} esu

(*S*,*S*,*S*)-**19**

Scheme 8

As a last example, we wish to present here the first case of a chiral enantiopure octupole (*S*,*S*,*S*)-**19** recently prepared by us[17]. In this organometallic compound three ferrocenyl groups are arranged at the 1,3,5 position of a central benzene core and each ferrocene is substituted by a electron-withdrawing dicyanovinylene group. Chirality arises from the homoannular ortho substitution on the ferrocenes (planar chirality) and we were able to prepare **19** as a single enantiomer by using an asymmetric synthesis of ferrocenes with planar chirality[24]. HRS measurement of **19** gave a β(0)=33x10^{-30} esu and it should be possible to improve this value by increasing the conjugation length between the electron rich ferrocenes and the acceptor groups and by using stronger acceptors.

In conclusion, we can see that despite the relative youth of octupole theory, many original structures as well as optimised hyperpolarisabilities have already been reported. Efforts should now focus on the incorporation of octupolar chromophores into efficient NLO active materials. As we already quoted before, one possibility relies on the engineering of non-centro symmetric crystals[6]. Another pathway relies on the orientation of octupolar molecules into solid matrix using optical poling technics. The first examples have been recently published in the case of the molecule of violet crystal[25].

References

[1.] *Nonlinear Optical properties of Organic Molecules and Crystals*, Eds Chemla, D.S. and Zyss, J., 1987, Academic Press, New York.
[2.] *See references in:* Blanchard-Desce, M.; Alain, V.; Bedworth, P.W.; Marder, S.R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S. and Wortmann, R. 1997, *Chem. Eur. J.*, 3, 1091.
[3.] Ledoux, I.. Zyss, J.; Siegel, J.S.; Brienne, J. and Lehn, J-M. 1990, *Chem Phys. Lett.*, **172**, 440.
[4.] Voigt-Martin, I.G.; Li, G.; Yakimanski, A.; Schulz G. and Wolff, J.J. 1996, *J. Am. Chem. Soc.*, **118**, 12830.
[5.] Joffre, M.; Yaron, D.; Silbey, R.J. and Zyss, J. 1992, *J. Chem. Phys.*, **97**, 5607.

[6.] Thalladi, V.R.; Brasselet, S.; Weiss, H.-C.; Bläser, D.; Katz, A.K.; Carrel, H.L.; Boese, R.; Zyss, J.; Nangia, A. and Desiraju, G.R. 1998, *J. Am. Chem. Soc.*, **120**, 2563.

[7.] a) Therhune, R.W.; Maker, P.D. and Savage, C.M. 1965, *Phys. Rev. Lett.*, **14**, 681. b) Maker, P.D. 1970, *Phys. Rev. A*, **1**, 923.

[8.] Clays, K. and Persoons, A. 1991, *Phys. Rev. Lett.*, **66**, 2980.

[9.] Zyss, J.; Dhenaut, C.; Chauvan, T. and Ledoux, I. 1993, *Chem. Phys. Lett.*, **206**, 409.

[10.] Morrison, I.D.; Denning, R.G.; Laidlaw, W.M. and Stammer, M.A. 1996, *Rev. Sci. Instrum.*, **67**, 1445. See also for dipolar molecules Flipse, M.C.; de Jonge, R.; Woudenberg; R.H.; Marsman, A.W.; van Walree, C.A. and Jenneskens, L.W. 1995, *Chem. Phys. Lett.*, **245**, 297.

[11.] Ref. 10 and refs therein.

[12.] Zyss, J. and Ledoux, I., 1994, *Chem. Rev.*, **94**, 77; See also Zyss, J. 1991, *Nonlinear Opt.*, **1**, 3.

[13.] a) Verbiest, T.; Clays, K.; Samyn, C.; Wolff, J.; Reinhoudt, D. and Persoons, A. 1994, *J. Am. Chem. Soc.*, **116**, 9320. b) Ray, P.C. and Das, P. K. 1995, *Chem. Phys. Lett.*, **244**, 153. c) Wortmann, R.; Glania, C.; Krämer, P.; Matschiner, R.; Wolff, J.J.; Kraft, S.; Treptow, B.; Barbu, E.; Längle, D. and Görlitz, G. 1997, *Chem. Eur. J.*, **3**, 1765.

[14.] Stadler, S.; Feiner, F.; Bräuchle, Ch.; Brandl, S. and Gompper, R. 1995, *Chem. Phys. Lett.*, **245**, 293.

[15.] Whitthall, I.R.; Humphrey, M.G.; Houbrechts, S.; Maes, J.; Persoons, A.; Schmid, S. and Hockless, D.C.R. 1997, *J. Organomet. Chem.*, **544**, 277.

[16.] Sastre, A.; Torres, T.; Díaz-García, M.A.; Agulló-López, F.; Dhenaut, C.; Brasselet, S.; Ledoux, I. and Zyss, J. 1996, *J. Am. Chem. Soc.*, **118**, 2746.

[17.] Riant, O.; Brasselet, S.; Ledoux, I.; Lefloch, F. and Zyss, J. *to be published.*

[18.] Zyss, J.; Van, T.C.; Dhenaut, C. and Ledoux, I. 1993, *Chem. Phys.*, **177**, 281.

[19.] Verbiest, T.; Clays, K.; Persoons, A.; Meyers, F. and Brédas, J.L., 1993, *Optics Lett.*, **18**, 525. b) Luo, Y.; Cesar, A. and Ågren, H, 1996, *Chem. Phys. Lett.*, **252**, 389.

[20.] Blanchard-Desce, M.; Baudin, J.-B., Ruel, O.; Jullien, L.; Brasselet, S. and Zyss, J. 1998, *Optic. Mat.*, **9**, 276.

[21.] Lambert, C.; Schmälzin, E.; Meerholz, K. and Bräuchle, C., 1998, *Chem. Eur. J.*, **4**, 512.

[22.] Dhenaut, C.; Ledoux, I.; Samuel, I.D.W.; Zyss, J.; Bourgault, M.; Le Bozec, H. and Zyss, J. 1995, *Nature*, **374**, 339.

[23.] Lequan, M.; Branger, C.; Simon, J.; Thami, T.; Chauchard, E. and Persoons, A. 1994, *Adv. Mater.*, **6**, 851.

[24.] a) Riant, O.; Samuel, O. and Kagan, H.B.; 1993, *J. Am. Chem. Soc.*, **115**, 5835. b) Riant, O.; Samuel, O.; Flessner, T.; Taudien, S. and Kagan, H.B., 1997, *J. Org. Chem.*, **62**, 6733.

[25.] a) Nunzi, J.M.; Charra, F.; Fiorini, C. and Zyss, J., 1994, *Chem. Phys. Lett.*, **219**, 349. b) Fiorini, C.; Charra, F.; Nunzi, J.M.; Samuel, I.D.W. and Zyss, J. 1995, *Optics Lett.*, **20**, 2469.