Display and Imaging, Vol. 2, pp. 197–206
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Strong Electron-withdrawing Heterocycles in Recent Nonlinear Optics Applications[†]

PIERRE AUDEBERT

PPSM, UMR 8531, Ecole Normale Supérieure de Cachan, Université de Paris-Saclay, 61 Av. du Pt Wilson, 94235 Cachan, France; E-mail: audebert@ppsm.ens-cachan.fr

Received: September 20, 2016. Accepted: October 27, 2016.

In this short review article, are recalled the most important recent findings on the use of highly electrodeficient heterocycles in nonlinear optics (NLO) Rather than making an extensive citation report, the author tends to focalize on the most striking challenges, and the new innovative attractors, giving a large place to modern challenges in NLO, like tow-photon absorption (TPA). Emphasize is put on demonstrating how the dimensionality of new NLO molecules, by changing the relative donor/attractor ratio, increases the interest of using highly accepting heterocycles. In this brief survey, are also evoked the importance of emerging fields for "recycling" old concepts, like modern all-organic photovoltaics and delayed fluorescence.

Keywords: NLO, electron-withdrawing heterocycles, push-pull molecules, two-photon absorption (TPA), triazines, tetrazines, triazoles, conjugated molecules, delayed fluorescence, photovoltaics

1. INTRODUCTION

As it could be expected, the field of research on molecules with a strong intermolecular charge transfer has relatively come to a pace lately, and therefore the quest of strong acceptors has slowed down; this is due to the decreasing interest for the molecules exhibiting a high second-order NLO activity (high β molecules). On the other hand the quest for donor compounds is still active, mainly because of the incentive of two-photons absorbing molecules, especially in the field of near IR for biology-related applications. Meanwhile, excellent acceptors have been dis-

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[†] The research leading to these results received funding from the H2020-MSCA-ITN-2015/674990 project "EXCILIGHT".

covered, and reviewed in many excellent articles (1). The quest for strong acceptors has therefore been recently more focused on molecules featuring acceptors (resp. donors) of different symmetry; however, a couple of new “simple” acceptors, like iodoniums, have appeared relatively recently.

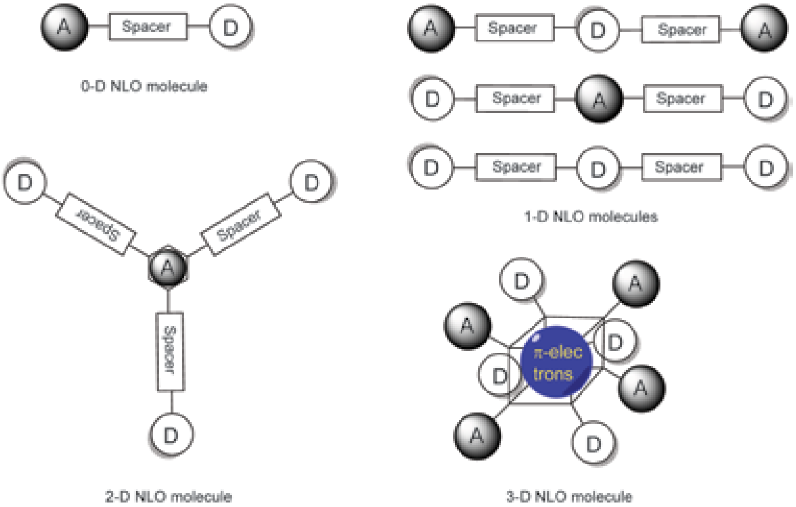
Since the easiest way to provide an attracting moiety with symmetry different from purely linear is an electrodeficient heterocycle, this short review will mainly focus on heterocyclic acceptors. This is not only for the reasons mentioned above, and because this is a relatively new field compared to old-style acceptors like tricyanoethylene, but also because the aromatic character of these heterocycles opens new possibilities especially in emerging fields like delayed fluorescence (2), or two-photons (2-PA) absorbers (3). After a short remainder of traditional strong acceptors which first emerged, and their applications (mainly in second order NLO) this review will deal with the modern heterocyclic strong acceptors, essentially azines and polyazoles. The diketopyrrolopyrrole moiety, which has been already largely, commented in short reviews, and which is not an especially strong acceptor, will not be covered by this review. Similarly, the dinitrobenzene acceptor, which is indeed moderately strong, has been so frequently investigated in the 80s and early 90s, that it will be also almost excluded from this record.

2. HISTORICAL CONTEXT

Before commenting on the results and the new acceptors used for NLO, it is necessary to recall the historical context. Until the late 90’s, the only molecules and systems to have been envisaged by researchers were “zero-dimensional” molecules, namely a donor moiety linked with an acceptor moiety through a conjugated spacer. (Scheme 1) The field has been reviewed quite regularly in this field (ref 1 and refs therein). The extension of dimensionality has reached the domain of 2nd order NLO, with the introduction by Zyss et al. of the concept of octupoles, which was the first, and extremely promising at the time, attempt to go beyond simple D-A molecules (4). Later, it was suggested that 3rd order NLO (namely 2-photons absorption (designed as TPA in the following) and optical Kerr effect, which are present even in symmetrical molecules) could be envisaged, and even enhanced with more complicated molecules, which extended the scope for molecules with strong donors and acceptors (5). Interestingly, the geometry of the molecules concerned was other than just the D-A type, or even the C3 symmetrical three-fold symmetry (planar octupoles). This opened the way for the for the introduction of the dimensional concept for charge-transfer molecules, that is, where the charge transfer path extends along one dimension, or within two, or three space dimensions.

The concept of what I am suggesting with increasing the dimension of a D-A type is exemplified (not extensively) in Scheme 1.

Scheme 1 illustrates this concept, notwithstanding that there are many more possibilities for 2-D and 3-D molecules. It should be noted that several works,



SCHEME 1.
Illustration of the dimension concept in NLO molecules trough classical (non-limitative!) examples, generally reading.

especially from the J.-L. Brédas group (6), emphasize that very strong donor and acceptors are not the solution to increase the β values of simple D-A molecules; the charge transfer should be optimum, around 0.5 like in cyanines, to reach optimal values (among other variables like the conjugation extension, in fact). However, this is not such an easy goal to achieve with non-ionic compounds…

However, the situation changes with molecules of different geometries, the search for strong acceptors (and also donors, although this is out of our current topic) becomes a much more important challenge, since the ratio of A/D in a molecule which is different from the simple D-A arrangement can vary a lot, and therefore, stronger electron acceptors (resp. donors) can be needed in order to balance the charge transfer properly within a given molecule, if more than one donor is in balance with only one acceptor, like in a D-A-D molecule, or a threefold symmetry molecule with one acceptor and three donors.. Within the scope of the research of new molecules with different geometries, the quest for strong acceptors is therefore an interesting challenge.

3. STANDARD “0-D” PUSH-PULL MOLECULES AND EXTENDED “1-D” SYSTEMS.

3.1. Standard “0-D” D-A molecules featuring strong acceptors.

The search for standard dipoles has known its peak in the 90s, and has been reviewed several times since then (7). Beyond the old dinitrophenyl, it seems that

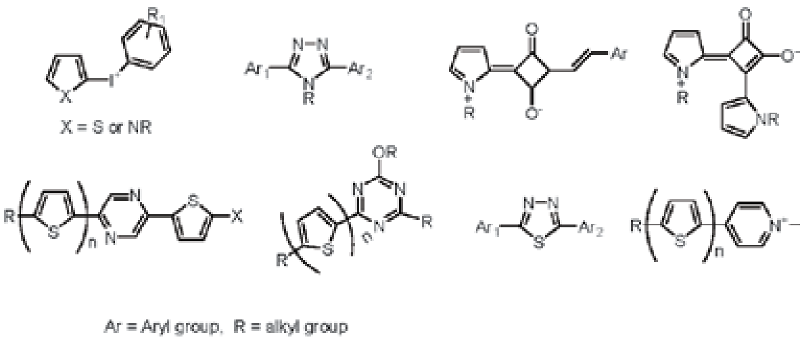


CHART 1.
Classical D-A molecules featuring new strong acceptors.

the favoured and most used acceptors, leading to the highest performances in β values are the barbiturate and thiobarbiturate on one hand (8), and the di- tricyanoethylene (TCNE) on the other hand (9). These moieties ally an extremely high electron deficiency to relatively easy functional group introduction (commercially available tetracyanoethylene reacts spontaneously with most electron-rich aromatics like thiophene to give the desired derivatives). Very high β values have been reached, especially by the group of M. Blanchard-Desce (8, 9).

The interest into 0-D NLO-phores has decreased, mainly because of the difficulty of building materials (polymers, crystals, etc…) with them, along with the relatively low temporal stability of the devices (mainly produced from doped or grafted polymers) which both are inferior to the performances of inorganic crystals like potassium triphosphate (KTP) (1 and refs herein). However, the quest of new acceptors continues somewhat, and original strong acceptors have emerged. Among them various ionic systems, like iodoniums (10) or squaraines (11), but several heterocyclic strongly deficient rings have also been used like thiadiazoles (12), triazoles (13-15), benzothiazoliums (16), pyridiniums and pyrimidines (17). The interest of these recently exploited strongly deficient heterocycles lies in the fact that their aromatic character provides them a better chemical stability than non-aromatic acceptors (eg TCE). In addition, compared to polynitrobenzenes, these are not explosive, and these are much more stable to weak nucleophiles than polycyanobenzenes. Chart 1 provides a non-exhaustive illustration of the aforementioned new D-A molecules featuring strong original acceptors.

3.2. "1-D" multi donor-acceptor molecules featuring strong acceptors, and twisted systems.

Quickly in the late 90s the quest for molecules featuring interesting multiple charge transfer started to develop, in order to meet different goals than simple 2^{nd} order hyperpolarisabilities (β or its macroscopic equivalent $\chi(2)$). The moti-

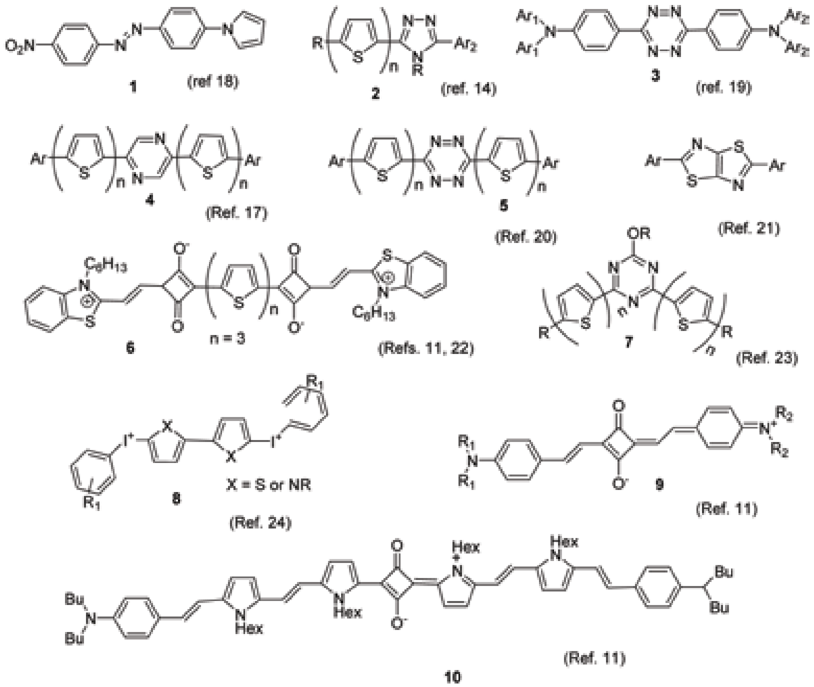


CHART 2.
CLASSICAL AND NON-CLASSICAL LINEAR OR BROKEN MOLECULES FEATURING STRONG ACCEPTORS.

vations clearly overcome even simple NLO, but there were extended to organic transistors (FET's) and, above all more recently organic photovoltaics. For this new class of molecules, most of the acceptors previously highlighted have been reused; the advantage of heterocycles is however more important, since most of them have at least two reactive carbons, through which to attach two donors, and sometimes more. The Chart 2 provides a selection of the structures mostly examined. Among these compounds, two properties have been more explored. 1) 3rd order NLO and 2) New materials for photovoltaics.

3.2.1. 3rd order NLO molecules and materials

A great limitation of second order active molecules is that they must be non-centrosymmetric. This is a serious limitation, especially considering that non-centrosymmetric molecules have in addition a tendency to organize into centrosymmetric systems in materials, in order to minimize the free enthalpy. On the other hand, this is not a requirement for 3rd order NLO, and it has been quickly recognized that A-D-A' and D-A-D' type molecules could be of great interest, even if completely centrosymmetric (A=A' or D=D') (25, 26). The published works have pointed mainly in two directions (opposite but complementary), high Kerr effect molecules and high 2-photon (TPA) absorbers. The optical Kerr effect designs the modulation of the refractive index at the same frequency, which depends on the real part of the γ of the molecule, at the same frequency. On the other hand, TPA (which is a 3rd order effect, contrariwise to where its name might mislead) is linked to the imaginary part of γ (27).

The third harmonic generation, an effect also linked to the same real part of γ, has been less investigated, probably because of higher difficulties in its observation (observation of Maker's fringes requires delicate equipment). Indeed, on the other hand γ at the same frequency is linked to the variation of the linear index with the intensity $n = n_0 + n_2 I$, where n, n_0 and n_2 represent respectively the measured refractive index, the linear refractive index (observed at low intensities) and the variation of the observed index with the intensity (28) . This is called the optical (or AC) Kerr effect (there is also a static Kerr effect where the refraction index modulation is proportional to the square of an applied static electric field); n_2 in turn is linked to the $\chi(3)$ by the relation: $n_2 = (3/4n_0)\chi(3)$, $\chi(3)$ being directly proportional to the molecular γ, through a relation which depends upon the Avogadro number and an orientation factor of the molecules in the optical beam field. n_2 can be easily determined by the Z-scan technique (29), while the TPA is also simple to estimate with a performing spectrometer, especially if it is associated with induced fluorescence, which is the most common way to estimate it. There is an important difference in the occurrence of these properties in molecules. While the real part of γ is specifically linked to the existence of a charge transfer in the molecule (a major parameter being the transition state (TS) dipole moment) on the other hand the TPA can be important in molecule without high charge transfer TS (eg D-D, D-D-D or more complicated conjugated molecules without acceptors (30)). TPA molecules are therefore much more common than Kerr effect molecules.

The first to have proposed A-D-A molecules for the Kerr effect are P. Audebert and H. Maillotte in the late 90's (25); at the time people were primarily interested in pure D-A molecules, and these authors started by showing that adding a small acceptor to a D-A molecule (converting it therefore to an a-D-A type) was beneficial to improve γ. This was confirmed shortly after in collaboration with the K. Ohta and K. Kamada group (26, 31). Later on the same group demonstrated that tetrazines substituted by ferrocene donors also displayed a correct γ (32). Meanwhile, other groups published similar results using different acceptors (33, 34).

On the other hand, TPA molecules had already attracted even more interest, especially because of their possible applications in biology. The first tendency was recycling again dipolar molecules (some of them behave quite well), then the research was more oriented towards electron-rich conjugated molecules. However, several A-D-A and D-A-D molecules were published, exhibiting good performances (33), especially by the groups of S. Marder and J. Perry, who especially produced the beautiful D-A-D squaraine **10,** the TPA of which attained 33,000 GM, one of the highest values ever reported (11).

More complicated molecules have also been produced and evaluated, and sometimes display quite interesting properties; however, the number of synthetic steps is rarely taken into account in the publications, which is nevertheless a severe limitation of these compounds.

3.2.2. Organic photovoltaics

Although this is borderline with the subject of this small review, it is interesting to notice that dipoles (34) and symmetrical A-D-A and D-A-D molecules have regained interest because of their efficiency in organic photovoltaic (OPV) devices. The interest of these molecular materials is that they are able to drive both electrons and holes, a feature highly interesting for this type of application. In this respect, the second families (A-D-A and D-A-D) are more interesting than simple dipoles, because they do not possess any dipole moment, and therefore can crystallize with respect to their electron-poor and electron-rich moieties facing each other, constituting therefore percolation pathways for both electrons and holes respectively in the same material. J. Roncali et al. recently detailed this in a particularly pertaining short review (35).

4. 2-D and 3-D structures

4.1.1. Octupoles

Since the brilliant demonstration by Zyss et al. (4) that 2nd order NLO effects were not to be found only with dipoles, but that there were cases of higher octupolar symmetry, some research was triggered in this direction. Octupoles should belong to three types of electronic configurations, cubic (Td space group), threefold (C3v or D3h space groups), or linear, but of a special type (Fig. 1), and a large interest has spread into these compounds.

I am not aware of a single publication of a real 1-D octupole (Fig 1) despite the interesting concept introduced by Zyss et al. (4) Indeed this is complicated to adjust, even coarsely, the strength of the respective donors and acceptors. However, there are numerous examples of 3-D octupoles (36-41), and in this chemistry the quest for strong acceptors is very important in structures where the acceptor is the central core of the octupole. Most examples are *s*-triazines, since triazine is a strong electron withdrawing ring with the appropriate symmetry. (Symmetrically, the structures where the central core is a donor requires a specially strong donor, except if the acceptors are also strong themselves).

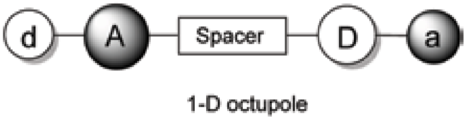


FIGURE 1.
Schematic picture of a 1-D octupole ; ideally, a/A and d/D charge balance should be equal to 1/3.

4.1.2. Other structures

A few works appeared trying to demonstrate the interest of different geometries (42); however, there is a lack of theoretical background in the field, and not so many attempts. However, nice and original twisted zwitterionic molecules were produced by T. Marks et al. (43) which displayed huge hyperpolarizabilities, this being due to the important charge separation in the weakly conjugated ground state, while electronic conjugation, concommitant with almost complete charge transfer is triggered by photoexcitation.

CONCLUSION

Altogether, the field of strong acceptors for NLO is shrinking, although new molecular structures are still being produced. The issue of the stability of organic compounds is still a recurrent problem, and inorganics have progressed meanwhile. However, it is still not forbidden to hope that new stable and interesting molecules can emerge. Some new very stable cores, like found in the heptazine derivatives (Fig. 2), at the frontier between inorganic and organic materials, still hold promises in my opinion. Recently, C. Adachi produced a tris(-*p*-fluoro-*m*-methyl-phenylheptazine) (44) (R1 = R2 = R3 = 3-fluoro-2-methylphenyl) as on Fig. 2 and a tris(N,N-bis(4-(tert-butyl)phenyl)aniline)heptazine (45) (R1 = R2 = R3 = N,N-bis(4-(tert-butyl)phenyl) aniline as on Fig. 2) which displayed high yield delayed fluorescence, a promising property! The search is still going on, but with more precise aims and requirements; interesting stable octupoles could likely be produced from this new 3-fold symmetry building block.

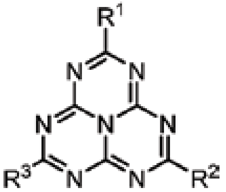


FIGURE 2.
The heptazine core

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