

New class of molecules predicted to exhibit non-linear optical properties

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The search for materials with non-linear optical (NLO) properties has been the subject of intense research, due to their application in a wide range of technologies, such as optical computing and optical communication [1–3]. Although several inorganic substances are known to exhibit NLO properties, macroscopic assemblies of organic molecules show great promise as new materials for building NLO devices, due to their fast response times [3].

Attempts at designing organic molecules with non-linear optical activity have traditionally used the push–pull model, where an electron donor group is connected to an electron-acceptor group through a spacer. In order to facilitate charge transfer between the donor and the acceptor groups, the spacer is usually a conjugate, planar or quasi-planar system.

Although molecules with reasonably large calculated hyperpolarizabilities (β and γ) can be designed following this procedure, at the crystalline level, the property can be cancelled due to anti-parallel centrosymmetrical stacking of the molecules induced by their planarity. A well known example of the failure of the push–pull design model is *p*-nitro-aniline, which was expected to have a large (at least for that time's standards) non-linear optical activity. Unfortunately, at the crystalline level the NLO activity vanishes. Some of the inconveniences of the 1-D π conjugated systems can be more or less circumvented by other arrangements such as 2-D Δ shaped molecules or 3-D tetrahedral DA compounds [4, 5].

Recently, Barbosa and Nascimento [6] proposed a new approach, where a non-planar unit, with high electron affinity, is used as the acceptor, to which several donors can be linked. This new strategy presents two great advantages over the traditional push–pull model: first, the non-planarity of the central acceptor unit reduces the probability of forming a centro-symmetric crystal; second, by properly choosing the type and number of donor groups, one can design molecules in which the octupolar components of the β and γ tensors can be maximized, according to the proposal of Zyss *et al.* [7]. The advantages of octupolar crystalline structures over the dipolar ones have been extensively discussed by Zyss *et al.* [8]. Using this new approach several derivatives of C_{36} exhibiting large values of β have been designed [6]. However, since the chemistry of C_{36}

is still in its infancy, it would be desirable to look for other classes of compounds that could be more easily synthesized and tested.

With this purpose in mind, we designed a new class of molecules, using as central acceptor units, cyano-substituted and fluoro-substituted ciclo-hexadienes, which exhibit considerably large electron-affinities.

The candidate molecules were designed using four different central acceptor unit (see Fig. 1):

The following donor units were used in this work (see Fig. 2):

They were connected to the molecule by substituting two of the hydrogen atoms bound to the sp^3 carbons in either the *cis* or *trans* position.

Geometries of the candidate molecules were optimized at the DFT/B3LYP(6-31G^{***}) level, using the JAGUAR package [9], and the vibration frequencies were calculated to check if the optimized structures correspond to a minimum in the potential energy hypersurface. The properties were computed at the time-independent CPHF/6-31G^{***} level [9, 10].

The separation of the dipolar and octupolar β components was carried out using the scheme proposed by Zyss *et al.* [7]. Although the dipolar-octupolar decomposition of the β tensor is not unique when both contributions are present in a molecule, this decomposition can be very helpful for our understanding on how the type and number of donor groups affect the values of both components.

The results for the calculated second hyperpolarizabilities (β) and molecular dipole moments (μ) are summarized in Tables I–III. The β and μ values are expressed in 10^{-30} esu and debye units, respectively.

We note that all the (etam)-substituted and (etdiam)-substituted molecules, with the exception of the ones showing a (2a)-*trans* or (2b)-*trans* framework, show large values of β .

The accuracy of the present calculations deserves some comments. Calculations performed at the highest level of theory presently available (coupled-cluster with singles, doubles, and corrections for triple excitations, CC-SDT) agree within 5–10% with the experimental results for β and γ [11, 12]. However, such calculations can only be performed for small molecules. Thus, for most of the molecules of interest for NLO, one has to rely on lower order approximations.

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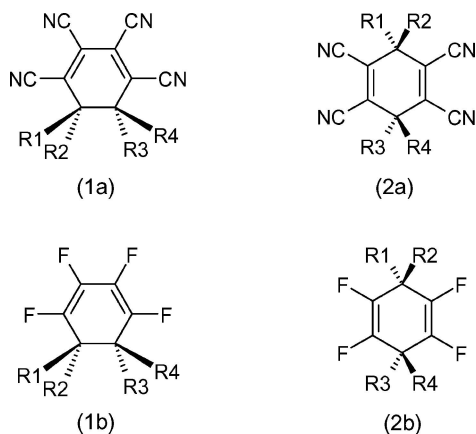


Figure 1 Molecular framework of acceptor central units proposed. 1,2,3,4-tetra-cyano-1,3-cyclo-hexadiene (1a); 1,2,3,4-tetra-fluoro-1,3-cyclo-hexadiene 1b, 1,2,4,5-tetra-cyano-1,4-ciclo-hexadiene (2a); 1,2,4,5-tetra-fluoro-1,4-cyclo-hexadiene 2b.

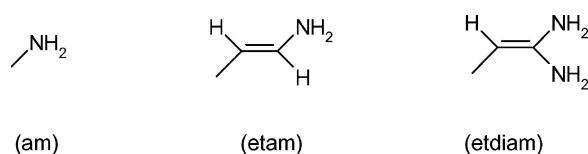


Figure 2 Framework of the proposed donor units. -Amine(am), -ethylene-2-(*trans*)-amine (etam), and -ethylene-2,2-diamine (etdiam).

Coupled-Perturbed HF calculations are known to produce values which are 30–40% smaller than the measured ones, depending on the size of the molecule and quality of the basis set employed. The results are substantially enlarged after vibration corrections [13] and correlation effects [14, 15] are taken into account. Therefore, we do not claim that our values of β are ac-

TABLE I Calculated dipole moments (debye)

		$\mu(x)$	$\mu(y)$	$\mu(z)$	$\mu(\tau\sigma\tau)$
(1a)- <i>cis</i>	am	-6.179	4.826	-2.995	8.393
	etam	-8.443	3.622	-4.070	10.048
	etdiam	-8.005	2.932	-3.718	9.301
(1a)- <i>trans</i>	am	-7.700	0.706	-4.208	8.803
	etam	-7.229	0.107	-4.113	8.318
	etdiam	-7.049	0.118	-4.013	8.112
(1b)- <i>cis</i>	am	-3.326	3.497	-2.028	5.235
	etam	-4.559	1.548	-2.139	5.268
	etdiam	-6.151	1.660	-1.227	6.488
(1b)- <i>trans</i>	am	-4.838	0.593	-2.587	5.518
	etam	-4.122	0.064	-2.348	4.744
	etdiam	-5.469	0.085	-3.126	6.299
(2a)- <i>cis</i>	am	-0.005	1.631	0.042	1.631
	etam	-0.016	5.951	-0.081	5.952
	etdiam	-0.039	7.343	-0.203	7.346
(2a)- <i>trans</i>	am	-0.043	0.011	0.021	0.012
	etam	0.006	-0.018	0.016	0.024
	etdiam	-0.003	0.010	-0.001	0.011
(2b)- <i>cis</i>	am	0.001	0.612	0.001	0.612
	etam	-0.011	2.829	-0.078	2.830
	etdiam	0.006	2.209	-0.117	2.212
(2b)- <i>trans</i>	am	0.011	-0.017	-0.010	0.022
	etam	0.003	-0.010	-0.021	0.023
	etdiam	-0.217	0.447	-0.905	1.032

TABLE II Dipolar components of the second hyperpolarizability tensor (a.u.)

β_{dipolar}		$\beta_{xxx} = \beta_{xyy} = \beta_{zzz}$	$\beta_{yyy} = \beta_{yxx} = \beta_{yzz}$	$\beta_{zzz} = \beta_{zxx} = \beta_{zyy}$
(1a)- <i>cis</i>	am	24.28	-30.97	-1.49
	etam	-104.76	227.90	-83.70
	etdiam	-86.39	179.55	-107.69
(1a)- <i>trans</i>	am	36.62	-3.35	19.96
	etam	-152.81	2.84	-87.04
	etdiam	-209.27	3.81	-119.63
(1b)- <i>cis</i>	am	45.48	-43.50	10.35
	etam	12.47	65.48	25.83
	etdiam	80.68	-1.91	30.21
(1b)- <i>trans</i>	am	62.39	-7.64	33.00
	etam	27.40	-0.21	15.39
	etdiam	70.93	-0.91	40.65
(2a)- <i>cis</i>	am	-0.39	25.38	0.29
	etam	-0.85	234.06	-3.86
	etdiam	1.22	137.07	-3.04
(2a)- <i>trans</i>	am	-0.01	-0.03	0.03
	etam	-0.20	-0.78	0.04
	etdiam	-0.52	-0.98	0.48
(2b)- <i>cis</i>	am	0.02	-2.81	0.04
	etam	-0.31	88.52	-2.70
	etdiam	-0.03	11.43	-0.73
(2b)- <i>trans</i>	am	0.00	0.11	-0.05
	etam	0.04	-0.23	-0.45
	etdiam	-5.86	-0.03	28.29

curate. On the other hand, we know for sure that they represent a lower bound to the correct values. Hence, the fact that this lower bound is already quite high, and that the correct values could be as much as 30–40% larger, certainly define these molecules as potential candidates for building NLO materials.

It is noteworthy that some of the candidate molecules show considerably large values of octupolar hyperpolarizabilities in more than one of the tensor components. This could lead to materials with more than one axis of optical activity. Also, due to the presence of large, out-of-plane substituents, it is less likely that these molecules will form centrosymmetric crystals.

A word about the stability and reactivity of the proposed molecules as also timing. The proposed molecules were built from stable compounds (Fig. 1), by replacing hydrogen atoms (see figure) by amino, ethylene-amine, and ethylene-diamine groups. The new bonds formed are also quite stable and there is no reason to believe that the built molecules would be unstable relative to their constituent atoms or smaller fragments. As far as their reactivity is concerned, the functional groups present in these molecules do not easily undergo chemical reactions. In fact, some molecules containing conjugated cyano [16, 17] and amino groups [18], designed according to the *push-pull* model, have been prepared. Therefore, we do not foresee any special difficulties for the preparation and handling of these molecules.

Thus, we propose that the molecules studied in this work, with the previously noted exceptions, are good candidates for producing very efficient NLO materials. We strongly hope that the possibility of using some of these derivatives for building new NLO materials will stimulate the synthesis of those molecules.

TABLE III Octupolar components of the second hyperpolarizability tensor (a.u.)

$\beta_{\text{Octupolar}}$		β_{xxx}	β_{xyy}	β_{xzz}	β_{yyy}	β_{yxx}	β_{yzz}	β_{zzz}	β_{zxx}	β_{zyy}	β_{zyz}
(1a)-cis	am	9.31	-7.88	-20.06	-1.96	36.11	-30.22	18.58	-56.73	0.98	21.13
	etam	-27.82	-127.60	211.05	24.25	25.45	-98.18	99.85	-36.63	-262.93	239.55
	etdiam	8.37	-169.71	144.59	-7.83	147.62	-124.12	129.09	-279.56	-107.71	339.56
(1a)-trans	am	2.78	-16.31	7.96	1.64	-8.09	3.16	16.59	-39.35	-10.43	11.05
	etam	117.14	-477.35	125.94	7.50	-83.42	60.91	155.88	-193.64	-274.00	72.57
	etdiam	118.46	-484.93	129.56	7.70	-139.59	116.49	166.26	-217.22	-281.58	137.93
(1b)-cis	am	2.68	6.13	-14.18	0.61	-13.41	11.59	-2.81	36.77	-28.34	-38.68
	etam	-27.40	29.80	52.39	26.26	-32.67	-46.10	16.03	58.48	-106.58	-2.67
	etdiam	-12.21	-9.58	46.20	28.63	22.67	-108.5	22.49	-76.85	9.39	-130.37
(1b)-trans	am	9.30	-34.61	6.73	4.66	-28.86	14.89	-11.56	57.91	-23.22	1.45
	etam	45.93	-184.19	46.40	2.91	-30.17	21.43	26.37	27.00	-106.11	22.17
	etdiam	26.82	-105.68	25.22	1.81	22.13	-27.56	-1.98	66.73	-60.78	-41.52
(2a)-cis	am	-0.18	0.35	0.17	-20.5	61.81	-0.32	0.02	0.57	-0.64	46.25
	etam	-1.33	3.41	0.58	-101.25	407.47	-103.71	2.10	-8.18	1.87	-15.66
	etdiam	0.99	7.53	-10.51	-16.05	77.66	-29.51	0.86	-2.94	0.36	392.19
(2a)-trans	am	-0.07	0.47	-0.26	0.11	-0.30	-0.04	-0.08	0.23	0.02	0.43
	etam	0.65	-1.86	-0.08	0.07	-0.31	0.11	0.28	-1.18	0.32	0.19
	etdiam	0.58	-1.77	0.03	-0.21	0.60	0.01	-0.17	1.65	-1.13	-0.83
(2b)-cis	am	-0.04	0.06	0.05	-4.50	46.07	-32.57	-0.20	0.33	0.29	10.96
	etam	-0.99	1.94	1.02	-37.14	244.89	-133.47	3.84	-6.95	-4.57	-15.46
	etdiam	-0.03	-16.09	16.19	59.86	-69.49	-110.11	5.83	3.94	-21.44	-305.98
(2b)-trans	am	0.14	-0.44	0.01	-0.28	0.58	0.27	0.05	-0.23	0.08	0.08
	etam	0.33	-0.91	-0.08	-0.20	0.26	0.35	0.13	-0.26	-0.14	-1.59
	etdiam	-6.01	2.24	15.78	16.83	-24.34	-26.17	-36.05	156.23	-48.10	201.09

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