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Exploiting the Helical Motif for Enhanced Nonlinear Optical Response: Hyperpolarizability of Substituted *m*-Phenylene Oligomers

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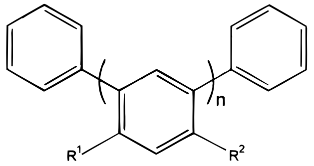
There is considerable interest in developing organic systems for use in nonlinear optical (NLO) applications.[1] The design strategy first involves the identification of a molecular candidate with a large hyperpolarizability, usually based on electronic factors. While many structural types have been studied, the most thoroughly examined systems involve push−pull substituted molecules with extended conjugation. Unfortunately, a sizable macroscopic susceptibility is not always obtained because of nonoptimal packing in the solid state. In centrosymmetric structures, the second harmonic generation is identically zero. While the problem can be overcome through poling or encapsulation in rigid polymeric matrixes, long-term thermal, photo, and oxidative stabilities are not easy to achieve.[2] We now consider an integrated approach in which electronic and molecular structures work in concert. Molecules with an intrinsic preference for adopting helical structures, but which also permit sufficient delocalization, are suggested as promising candidates for NLO applications.

Several organic compounds are known to form helices due to a combination of steric and torsional effects as well as intramolecular hydrogen bonding.[3] These include helicenes,[4] polypeptides containing α- as well as β-amino acids,[5] polyimines,[6] polyisocyanides[7] and -isocyanates,[8] substituted urea,[9] oligoanthranilamides,[10] etc. One approach to exploit the helical structure is to attach suitable NLO chromophores to the rigid backbone of the polymer to obtain a large coherent response, as successfully demonstrated with polyisocyanides.[11] A more direct strategy involves the design of helical structures with intrinsically large hyperpolarizability. Many helical substrates, including unsubstituted helicenes whose electro-optic properties were the subject of a recent theoretical study,[12] may lack the charge delocalization needed in the ground and excited states for effective nonlinear optical response. We discuss the hyperpolarizabilities of more strongly polarized systems which allow some conjugation.

In contrast to poly(*p*-phenylene) whose structures, properties, and potential as a high-performance material have been studied intensively in recent years,[13] the *meta*-analogues have attracted relatively less attention. Although the first synthesis was reported over 60 years ago,[14] structural information has been sparse. As is well-known, the rings in biphenyl prefer a twisted arrangement (ca. 45° in the vapor and solution phases).[15] Oligomeric *m*-phenylenes will have a helical shape if successive rings are twisted in the same sense.[16] Williams et al.[17] have confirmed the helical structure of *m*-deciphenyl and *m*-undeciphenyl $[C_6H_5(m\text{-}C_6H_4)_nC_6H_5$, $n = 8,9]$ from single-crystal X-ray study. Related compounds with heterocyclic rings have also been shown to have helical structures in the solid state.[18] We have investigated theoretically the hyperpolarizability of such structures of oligomeric *m*-phenylenes, $[C_6H_5(m\text{-}C_6H_4)_nC_6H_5$; $n = 4-7]$, (**1**), as well as their derivatives (**2**,**3**) containing donor and/or acceptor groups (amino and nitro/cyano groups, respectively). For effective push−pull interactions, the substituents have been placed *ortho* or *para* to the carbon atoms C_1 and C_3 connecting the oligomer chain, and consequently are *meta* with respect to each other. The chosen connectivity should permit optimal polarization of each ring as well as transmission of electronic effects along the chain. Additionally, oligomers with exclusively donor (**4**) or acceptor (**5**,**6**) groups were studied.



1: $R^1 = H$; $R^2 = H$;
2: $R^1 = NO_2$; $R^2 = NH_2$;
3: $R^1 = CN$; $R^2 = NH_2$;
4: $R^1 = H$; $R^2 = NH_2$;
5: $R^1 = NO_2$; $R^2 = H$;
6: $R^1 = CN$; $R^2 = H$;

For all the structures considered, the geometry was fully optimized at the AM1 level.[19] Molecular hyperpolarizability, β, was computed using the sum-over-states procedure.[20] The excited-state energies and wave functions were obtained through single and pair excitation configuration interaction spanning 18 frontier orbitals (PECI = 18).[21] The static hyperpolarizability, β_0, as well as resonance-enhanced value with excitation energy of 1.17 eV

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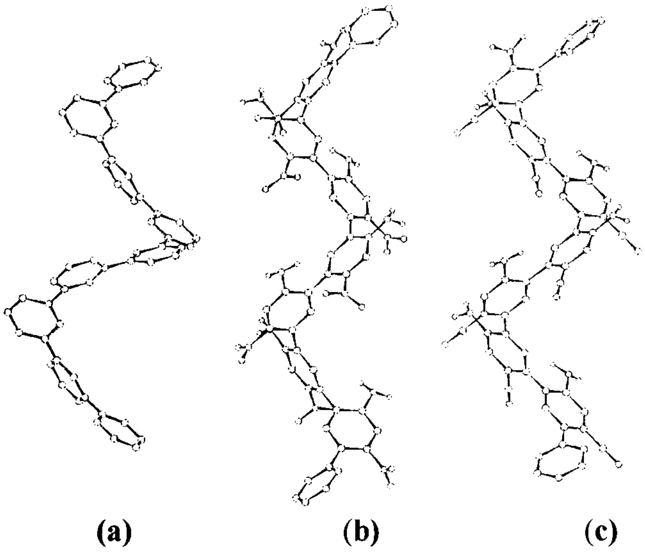

Figure 1. AM1 optimized geometries of **1**−**3** ($n = 7$).

(1064 nm) were computed. The tensorial components were converted to effective β_{vec} values in the usual manner.[20,21] The methodology employed has been validated through extensive comparisons with experiment and ab initio calculations on a number of conjugated systems.[21,22]

The optimized structures of the unsubstituted oligomers of *m*-phenylene (**1**) reveal the helical motif, the torsional angles about the formal single bonds being around 41°. A representative structure obtained for **1** ($n = 7$), shown in Figure 1a, is quite similar to the X-ray structure of *m*-deciphenyl.[17] The optimized structures of the substituted derivatives **2**−**6** retain the helicity, although the torsional angles are higher (average values, **2** 74°, **3** 62°, **4** 62°, **5** 61°, **6** 50°). Therefore, the steric perturbation due to substituents does not destroy the possibility of helical shape in these systems (Figure 1b,c).

The parent system is calculated to have relatively low β values (Table 1). This is due to the lack of electronic polarization, as is evident from the low values of dipole moment in the ground and excited states even in the large oligomer, **1** ($n = 7$). However, there is a remarkable increase in β value as the push−pull substituents are introduced. The computed β values increase rapidly with the chain length from $n = 3-6$ in $C_6H_5[m\text{-}C_6H_2(NH_2)(NO_2)]_nC_6H_5$ (**2**). A strong resonance enhancement is also computed in these systems based on the β values obtained with 1.17 eV excitation energy. Increasing the chain length further does not result in enhanced hyperpolarizability. In contrast to the molecular dipole moment, which keeps increasing with addition of rings, the β values reach a saturation value. The maximum $\beta_{1.17}$ value obtained for this series is 60×10^{-30} esu cm^{-5}.

Interestingly, the calculated β values obtained for $C_6H_5[m\text{-}C_6H_2(NH_2)(CN)]_nC_6H_5$ (**3**) are even larger, especially with $n = 6$ and 7. Up to the chain lengths considered, the NLO response has not attained saturation values. In **3** ($n = 7$), the value of $\beta_{1.17}$ is computed to be nearly 95×10^{-30} esu cm^{-5}. Despite its weaker electron withdrawing power, the cyano substituent is indicated to be more effective than the nitro group in inducing a large molecular hyperpolarizability in these substrates.

The hyperpolarizabilities of the derivatives containing only the donor group, $C_6H_5[m\text{-}C_6H_3(NH_2)]_nC_6H_5$ (**4**), or the acceptor groups, $C_6H_5[m\text{-}C_6H_3(NO_2)]_nC_6H_5$ (**5**) and $C_6H_5[m\text{-}C_6H_3(CN)]_nC_6H_5$ (**6**), provide further surprises. Besides being high, the β values do not saturate at the chain lengths considered in these systems as well. The magnitude of molecular hyperpolarizability is especially large in the amino compounds. Among all the systems studied here, **4** with $n = 7$ is calculated to have the highest $\beta_{1.17}$ value (110×10^{-30} esu cm^{-5}).

Table 1. Calculated Heats of Formation (kcal mol^{-1}), Hyperpolarizabilities (10^{-30} esu cm^{-5}), Ground State Dipole Moments (*D*) and Transition Wavelengths (nm) for **1**−**6**

	n	ΔH_f	β_0	$\beta_{1.17}$	μ	λ_{max}
1	4	150.2	0.8	1.0	0.1	288
	5	175.8	0.1	0.2	0.0	273
	6	201.5	0.1	0.2	0.0	278
	7	227.2	2.9	3.7	0.1	283
2	4	174.6	30.3	44.7	15.0	318
	5	207.5	38.2	56.0	21.0	320
	6	237.0	40.0	58.6	24.1	318
	7	268.1	40.0	60.2	27.8	318
3	4	279.7	28.4	41.4	10.8	328
	5	337.7	43.6	62.8	13.3	327
	6	395.7	59.8	83.8	16.0	330
	7	453.7	66.6	94.8	18.5	329
4	4	145.8	21.0	31.0	2.8	296
	5	170.5	39.2	56.2	2.3	292
	6	195.1	59.7	86.0	3.0	295
	7	219.8	77.3	110.5	3.7	294
5	4	187.3	11.6	16.2	12.0	291
	5	222.7	20.5	28.6	15.5	272
	6	258.1	29.8	41.7	19.1	268
	7	293.5	35.6	49.8	21.9	268
6	4	285.8	14.2	19.6	7.6	282
	5	345.6	16.4	23.4	9.3	288
	6	405.4	25.8	36.8	11.6	287
	7	465.1	41.4	57.8	13.7	283

Many of the features of molecular hyperpolarizabilities of **2**−**6** can be understood in terms of a combination of structural and electronic factors. The multiply substituted oligo(*m*-phenylene)s suffer strong steric repulsions. While helicity is maintained, the inter-ring torsion angles are enhanced, resulting in less effective extended conjugation. Further, the substituents are not optimally aligned, especially in derivatives **2** and **5**, in which the nitro groups are twisted significantly out of the phenyl plane. The cyano derivatives do not suffer these predilections and, hence, are computed to have relatively large β values.

The structures **2** and **3** are different from linearly conjugated systems, in which the push−pull effects can be orchestrated effectively. Due to the *meta*-connectivity, cross conjugation is unavoidable in poly(*m*-phenylene)s. The donor and acceptor substituents act on the same centers, C_1 and C_3, and as a result do not polarize the ring sufficiently strongly. Consistent with this interpretation, the calculated transition wavelengths, λ_{max}, are relatively insensitive to the chain length for all the oligomers considered (Table 1). Therefore, a single type of substituent, as in **4**, is computed to be more effective in inducing a large NLO response.

In summary, substituted poly(*m*-phenylene)s are suggested to be promising for NLO applications. A combination of push and pull groups is not the most effective in leading to a large hyperpolarizability. In addition to ring polarization, it is important to keep the twist angle between successive rings to a minimum. As a result, the presence of a single strong donor in each ring is ideal for a significant nonlinear optical response. The combination of low dipole moment and high hyperpolarizability is a particularly interesting feature of such systems. The helices are unlikely to pack antiparallel to each other. However, the systems may not be suitable for poling applications. Experimental studies would be of great interest, especially since efficient synthesis of substituted poly(*m*-phenylene) has been achieved recently.[23]

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