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Some organic and organometallic molecules with remarkably large second hyperpolarizabilities

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Abstract. The structure-polarization relationship has been investigated in a series of polyenes. Various conjugation patterns have been studied and their effect on the polarizabilities and hyperpolarizabilities has been commented upon. Two classes of conjugated oligomers have been shown to have very large second hyperpolarizabilities. It is shown that the known potential of the conjugated chains to lead to large nonlinearities is enhanced by substituting one or more hydrogen atoms with lithium. This interesting and useful point is documented by calculating the hyperpolarizabilities of several selected organolithium derivatives presenting a variety of molecular structures. The largest computed nonlinearity is $\gamma = 4 \times 10^7$ a.u., which is an exceptionally large value. The present computations have been performed using the semi-empirical approaches MNDO, PM3 and MNDO/d. This choice of well-tested semi-empirical models, in connection with the available literature values (theoretical and experimental), supports the validity of the reported findings.

Key words: Polarizabilities – Hyperpolarizabilities – Nonlinear optical materials

1 Introduction

The energy of a molecule in a static, uniform electric field may be expressed as a power series in the field [1]:

$$E = E^{(0)} - \mu_\alpha F_\alpha - \tfrac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \tfrac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \tfrac{1}{24}\gamma_{\alpha\beta\gamma\delta}F_\alpha F_\beta F_\gamma F_\delta \ldots \quad ,$$

where Greek subscripts denote cartesian components, a repeated index implies a summation and E, $E^{(0)}$, μ_α, $\alpha_{\alpha\beta}$ $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are the unperturbed energy, the perturbed energy, the dipole moment, the polarizability, the first hyperpolarizability and the second hyperpolarizability components, respectively. Physically the tensor components describe the distortion of the charge distribution due to the applied field [1, 2].

The tensor elements are derivatives of the energy (or the dipole moment) with respect to the electric field components. These partial derivatives can be determined by using finite difference or analytical methods [2, 3]. Hyperpolarizabilities, besides their importance as fundamental molecular properties [1a, b], are of crucial importance for the design of materials with many applications (e.g. construction of devices for high-speed transmission and storage of data etc. [4]). The need for such materials is well documented. In fact Garito et al. [5] stated that "third order effects in currently available materials are still orders of magnitude away from realistic device applications".

Thus the objectives of the present work are to contribute to the study of the structure-polarization relationship and to reveal some highly polarizable structures. More specifically, we have performed a comparative study of some derivatives with various patterns of conjugation. We sought those molecular geometries which lead to even larger hyperpolarizabilities than the corresponding polyenes, which are considered to have among the largest third-order nonlinearities ever measured [6]. Two classes involving sulphur have been selected. The first has an extended conjugated backbone and the second is based on tetrathiafulvalene (TTF).

The lithium molecule (Li_2) is known to have very large second hyperpolarizability, γ [7]. Taking this observation into account, we selected and designed several lithium-containing derivatives to investigate, in a systematic and comprehensive way, the effect of lithium on the polarizability and in particular the second hyperpolarizability of the substituted derivatives. Among these are some lithiated derivatives of C_2H_4, C_6H_6, TTF and conjugated oligomers.

The present study has been performed using several semi-empirical methods (MNDO, PM3 and MNDO/d) in a comparative way to safeguard the validity of the findings. In addition, results found in the literature, experimental and theoretical, using various methods (Tables 1, 2), are compared with those reported in the present work (Tables 3, 4).

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2 Computational methods

Of primary importance for the present work are the trends and differences in the properties, because these are necessary for discussing the structure-polarization relationship. Understanding of this relationship helps to recognize the patterns or motifs likely to be associated with large hyperpolarizabilities. Thus, in the present study, in order to safeguard the validity of our findings, we have used, in a comparative way, the following well-tested, semi-empirical methods.

2.1 MNDO

Most of the computations involving H, Li, C and S have been performed with the MNDO [8] method, since this approach is used by many research groups for a wide variety of applications, including hyperpolarizabilities [9], and thus constitutes an easily accessible reference technique (Tables 3–9). In general, this technique gives, reasonably accurate polarizability values, because it includes a correction factor which reduces the error in the MNDO values [8c]. This is clearly shown by comparing the MNDO and PM3 values of $C_{2n}H_{2n+2}$, n = 1–3, with the available experimental data (Table 1).

2.2 MNDO/d

This method [10] is more appropriate for sulphur-containing derivatives, since it uses *d* orbitals (Tables 3, 4, 9). For completeness it should be added that *d* functions on *S* have also been implemented by other semi-empirical techniques [11a, b].

2.3 PM3

Among the neglect of diatomic differential overlap (NDDO) approaches widely used, i.e. MNDO, AM1 and PM3, only the former had been parameterized for Li. The Li/MNDO set, besides its recognized usefulness in many applications, has also been criticized [11d] (e.g. for overestimating the C-Li and H-Li interactions [11d]). A useful contribution has been made by Anders et al. [11d], who optimized a set of lithium parameters for the PM3 method. They demonstrated that for the 18 selected reference compounds, Li/PM3 performed better than the Li/MNDO on the computation of heats of formation and bond lengths. Both methods determined ionization potentials and dipole moments with comparable accuracy [11d]. A detailed description of the methods presented briefly above, which have been employed in this work, can be found in various studies, e.g. Refs. [3b, 8a, 10, 11c,d].

In Table 6, the polarizability α and the second hyperpolarizability γ of Li_2 [7] and LiH [11e] are presented. These properties have been computed with MNDO [10], PM3 [11c, d] and an ab initio method, MP4[SDTQ] [11f] employing large basis sets. It is observed that the Li/PM3 results are of better quality than those determined using the Li/MNDO method. This is likely to be due to the more careful and successful parameterization of the former in comparison to the latter technique.

The polarizabilities and hyperpolarizabilities presented in this work are static and have been computed with the finite-field method, implemented in MOPAC [3b, 8b] except for the results produced using the MNDO/d technique, which have been calculated analytically [10c]. The property values presented in Tables 1–9 are given in atomic units (a.u.) [12]. The coordinates of all the molecules studied in this work can be provided on request.

3 Results and discussion

3.1 Literature survey

There is a large number of articles on the polarizabilities and hyperpolarizabilities of polyenes using ab initio and semi-empirical methods. Here we briefly review the ones relevant to the aims of the present study. Das and Dudis [9a] used a simplified and approximate ab initio theory in which the properties (α, γ) are determined in terms of local and nonlocal contributions. They determined α and γ of C_6H_6 (benzene) and $C_{2n}H_{2n+2}$, n = 2–11. They compared their $\alpha/2n$ and $\gamma/2n$ with MNDO calculated values and found a close agreement. However, as 2n increases a discrepancy appears. Das and Dudis [9a] found saturation for 2n = 44 in agreement with experimental observations.

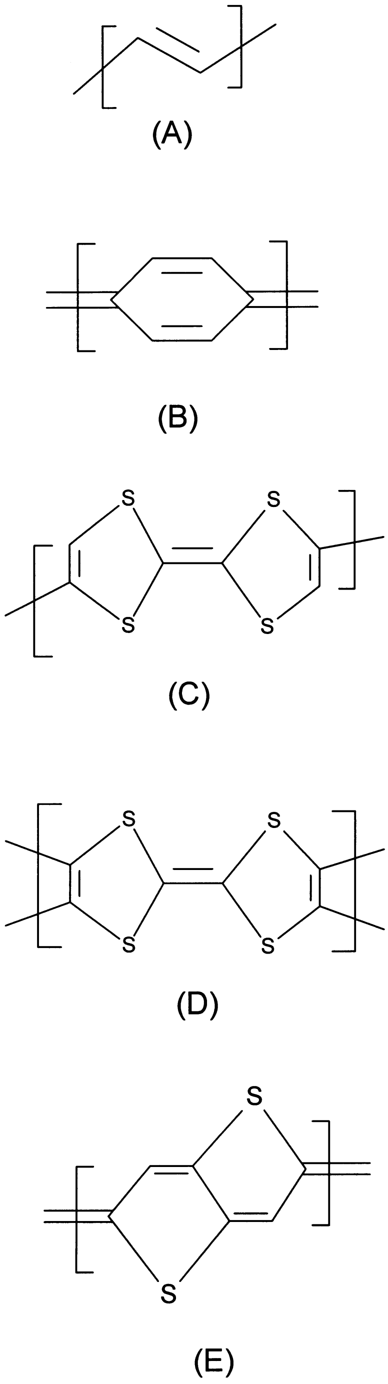


Fig. 1A–E. The structure of the oligomers considered in this work

Table 1. Literature values for the polarizability α of $C_{2n}H_{2n+2}$ (in a.u.)

n	VEH-SOS[a]	CHF-PT-EB-CNDO[b]	6-31G[c]	6-31G*[c]	6-31G+PD[c]	Exp.
1		29.71				28.48[d]
2	37.12	69.73	42.82	43.24	53.27	58.3[e]
3	74.71	128.19	73.09	73.58	87.92	87.46[f]
4	139.02		109.84	110.36	129.02	
5	209.01		152.15	152.60	175.69	
6	289.79		198.89	199.21	226.81	
7	382.65		248.94	249.09	281.25	
8	485.23		303.20	302.97	339.86	
9			358.16			
10			416.35			
11			473.27			

[a] Ref. [6b]
[b] Ref. [22]
[c] Ref. [2]
[d] Ref. [32]
[e] Cited by Hurst et al. in Ref. [2]
[f] Cited by Huang et al. in Ref. [20f]

Table 2. Literature values for the second hyperpolarizability γ of $C_{2n}H_{2n+2}$ (in 10^4 a.u.)

n	SSH-SOS[a]	VEH[b]	CHF-PT-EB-CNDO[c]	6-31G[d]	6-31G*[d]	6-31G + PD[d]	Exp.
1			0.8263				0.90 ± 0.02[e]
2	0.27	0.101	3.3447	0.1098	0.1055	1.4846	2.74 ± 0.16[e,f]
3	2.819	1.275	7.2137	0.9878	0.9196	3.5118	8.97 ± 0.83[e,g]
4	11.78	7.286		4.0775	3.7637	8.2212	
5	32.44	25.31		11.4624	10.5242	17.8443	
6	69.32	66.22		25.3843	23.1979	34.5721	
7	124.9	143.2		47.6398	43.3515	60.3537	
8	199.2	269.7		80.8879	73.2489	97.6279	
9	290.7	457.8		123.0311			
10	396.8	716.3		178.0479			
11	514.4	1051		238.0428			

[a] The Su-Schrieffer-Heeger (SSH) Hamiltonian has been used. Double excited states in a sum-over-states (SOS) approach have been taken into account [6b, 33]
[b] The valence effective Hamiltonian method has been employed [6b]
[c] An extended basis CNDO (EB-CNDO) wave function has been used. The properties have been computed by using the McWeeny's et al. coupled Hartree-Fock perturbation theory (CHF-PT) [3c, d, e]
[d] Ref. [2]
[e] Values determined in the gas phase, employing DC electric-field induced second harmonic generation [34]
[f] This gas involves *cis* (< 1%) and *trans* (99 + %) isomers [34]
[g] 1,3,5-Hexatriene involves *cis* (10–40%) and *trans* (60–90%) isomers

Table 3. The polarizability of some oligomers as a function of the number of double bonds. The structures of the oligomers (***A***, ***B***, ***C***, ***D*** and ***E***) have been fully optimized and their properties have been determined using the methods defined in this table

Number of double bonds	α/a.u.							
	A		B	C	D	E		
	MNDO	PM3	PM3	MNDO	MNDO	MNDO	PM3	MNDO/d
1	26.2	15.0						
2	55.1	35.3						
3	90.8	62.0						
4	132	94.1				198	179	206
5	177	130						
6	225	169				347	339	398
7	276	211	214		357			
8	328	254				541	561	675
9	381	298		401	484			
10	434	343	440			778	851	1060
11	489	388			613			
12	544	434		547		1060	1210	1560
13	599	481	805					
14	654	528						
15	710	574		693				

Table 4. The second hyperpolarizability of some oligomers as a function of the number of double bonds. The structures of the oligomers (***A***, ***B***, ***C***, ***D*** and ***E***) have been fully optimized and their properties have been determined using the methods defined in this table

Number of double bonds	$\gamma \times 10^{-4}$/a.u.							
	A		**B**	**C**	**D**	**E**		
	MNDO	PM3	PM3	MNDO	MNDO	MNDO	PM3	MNDO/d
1	−0.02[a]	0.01						
2	0.43	0.39						
3	3.01	2.54						
4	10.3	8.76				6.89	8.92	11.5
5	24.9	21.5						
6	48.3	42.5				35.4	47.1	51.3
7	81.1	72.6	14.2		16.5			
8	123	112				131	192	189
9	173	159		17.6	26.4			
10	230	214	106			380	630	619
11	292	275			38.0			
12	360	341		29.5		908	1750	1850
13	432	412	577					
14	508	487						
15	586	564		39.3				

[a] It is noted that MNDO gives the wrong sign for γ of C_2H_4 (Table 2)

Table 5. The ratios R_α and R_γ $R_\alpha = \alpha(\mathbf{X})/\alpha(\mathbf{A})$ and $R_\gamma = \gamma(\mathbf{X})/\gamma(\mathbf{A})$, of the oligomers ***B***, ***C***, ***D*** and ***E*** where the compounds ***A*** and **X** = ***B***, ***C***, ***D*** or ***E***, are defined in Fig. 1

Number of double bonds	R_α				R_γ			
	B[a]	**C**[b]	**D**[b]	**E**[c]	**B**[a]	**C**[b]	**D**[b]	**E**[c]
1								
2								
3								
4				1.50 1.56				0.67 1.12
5								
6				1.54 1.77				0.73 1.06
7	1.01		1.29		0.20		0.20	
8				1.65 2.06				1.07 1.54
9		1.05	1.27			0.10	0.10	
10	1.28			1.79 2.44	0.50			1.65 2.69
11			1.25					
12		1.01		1.94 2.87		0.08	0.1	2.52 5.14
13	1.67				1.40			
14								
15		0.98				0.07		

[a] The PM3 [11c, d] method has been used for the determination of these ratios

[b] The MNDO [8] approach has been employed for the calculation of these ratios

[c] For each compound two ratios are presented, the first of which has been determined using MNDO [8] and the second using MNDO/d [10]

Pierce [13] computed $\gamma(0;\ 0,\ 0,\ 0)$, $\gamma(-2\omega;\ \omega,\ \omega,\ 0)$ and $\gamma(-3\omega;\ \omega,\ \omega,\ \omega)$ using a procedure according to which γ is partitioned into γ_σ (σ-electron contribution) and γ_π (π-electron contribution). The first term is evaluated employing a bond-additivity model and γ_π by the INDO-SDCI. The γ expression of Orr and Ward [14] is used (sum-over-states). Among the systems they have considered is $C_{2n}H_{2n+2}$, n = 1–4. Matsuzawa and Dixon [15] used the PM3 method to compute α, β and γ of a series of polyenes and other extended n systems. They compared their results with those determined experimentally using EFISH and THG techniques and found that the calculated values reproduce the magnitude of γ. Conjugated polyenes were studied by Chen and Mukamel [16] using the density matrix approach. They employed the average bond order alternation to discuss the variation of α, β and γ of these derivatives.

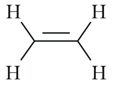
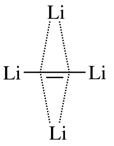
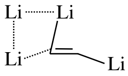
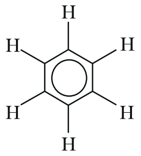
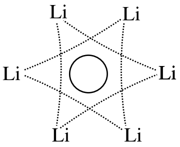
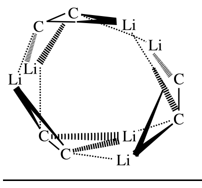
Albert et al. [17] computed the polarizabilities and hyperpolarizabilities of $C_{2n}H_{2n+2}$, n = 1–5, using the πSDCI method, in which the basis set involves a set of determinants of singly and doubly excited configurations between π orbitals. Shuai and Brédas [6b] computed static and dynamic α and γ values at $C_{2n}H_{2n+2}$, n = 2–15, using the valence effective Hamiltonian connected with the sum-over-states (SOS) approach. Heflin et al.

Table 6. Comparison of α and γ values for Li_2 and LiH, determined using MNDO, PM3 and ab initio MP4[SDTQ] with large basis sets

Compound	α/a.u.			$\gamma \times 10^{-3}$/a.u.		
	MNDO	PM3	MP4[SDTQ]	MNDO	PM3	MP4[SDTQ]
Li_2	101	198	204^a	−0.013	930	910 ± 50^a
LiH	10.9	14.5	27.15 ± 0.05^b	11.6	21.8	90.7 ± 5.6^b

[a] Ref. [7]
[b] Ref. [11f]

Table 7. The effect of lithiation of C_2H_4 (ethylene) and C_6H_6 (benzene) on their polarizability and hyperpolarizability

Molecule[a]	MNDO		PM3	
	α/a.u.	$\gamma \times 10^{-4}$/a.u.	α/a.u.	$\gamma \times 10^{-4}$/a.u.
	26.2^b 26.1^c	-0.02^b -0.02^c	15.0^b 15.3^c	0.01^b 0.01^c
	119^b	23.0^b		
			288^b	194^b
	68.8^b 67.7^c	0.14^b 0.14^c	45.6^b 45.5^c	0.15^b 0.15^c
	172^b 174^d	12.3^b 14.2^d	232^b 211^d	110^b 79.9^d
	91.5^e	3.22^e	105^e	7.95^e

[a] Optimization of the geometry of C_2Li_4 gave different structures with MNDO and PM3
[b] The geometry has been optimized using the same theoretical model which has been used for the calculation of α and γ
[c] The experimental geometry has been used for the computation of α and γ [35]
[d] The SCF/TZP structure (D_{6h}) reported by Xie and Schaefer has been used for the computations [26a]
[e] The SCF/TZP structure reported by Smith [26b] has been used. This is number 5 in Table 1 of Ref. [26b]

[18] computed $\gamma_{xxxx}(-3\omega; \omega, \omega, \omega)$ of $C_{2n}H_{2n+2}$, n = 2–8, for *all-trans*-and *cis*-transoid conformations. They used a complete neglect of differential overlap/spectroscopic (CNDO/S) method connected with CI.

The full spectrum of $\chi^{(3)}(3\omega; \omega, \omega, \omega)$ in polyacetylene employing an infrared free-electron laser was measured by Fann et al. [6d]. They found that $\chi^{(3)} \approx 10^{-8}$ esu at 0.6 eV. For the transparent gap region of semiconductors this was the largest-ever electronic value measured for $\chi^{(3)}$ [6d]. The γ value of *p*-benzoquino-dimethane was computed by McIntyre and Hameka [19], who used the Hückel approximation for the computation of the molecular orbitals. There are many more studies which deal with several aspects of the polarizabilities and/or the hyperpolarizabilities of polyenes, some of which are given in Ref. [20]

Table 8. The polarizability and second hyperpolarizability of some lithiated oligomers as a function of the number of double bonds. The structures of the lithiated oligomers ***B*** and ***E*** (Fig. 1) have been fully optimized and their properties have been determined using the PM3 method. The properties of the polyenes $C_{2n}H_{2n+2}$ are presented for purposes of comparison

Number of double bonds	**A**		**B**		**E**	
	α/a.u.	$\gamma \times 10^{-4}$ /a.u.	α/a.u.	$\gamma \times 10^{-4}$ /a.u.	α/a.u.	$\gamma \times 10^{-4}$ /a.u.
4	94.1	8.76			390	864
6	169	42.5			622	881
7	211	72.6	415	286		
8	254	112			949	1260
10	343	214	741	781	1380	2180
12	434	341			1940	4090
13	481	412	1280	2640		

3.2 Structures with C, S and H

We have computed the polarizability, α and the hyperpolarizability, γ, of several classes of polyenes (Fig. 1**A**–**E**), presenting various patterns of conjugation. Three of these families of molecules involve sulphur as well (**C**–**E**). The properties have been calculated using MNDO, PM3 and MNDO/d, since the MNDO level of approximation has been shown to be adequate for the determination of the hyperpolarizabilities of conjugated systems [9]. The structures employed for the computation of α and γ have been optimized with the semi-empirical model used for the calculation of the above properties.

First, we will discuss our results for $C_{2n}H_{2n+2}$ (**A**). The hyperpolarizabilities, γ, of $C_{2n}H_{2n+2}$, define a measure, since they are among the largest ever observed [6], and we aim at designing or recognizing structures with even larger response. The geometric elements of all the molecules considered in this work have been fully optimized at the level of approximation for which the properties are presented.

It is shown that MNDO gives satisfactory polarizability values for $C_{2n}H_{2n+2}$, as demonstrated by comparing the computed values with the experimentally determined data for C_2H_4, C_4H_6 and C_6H_8 (Table 1). The average error is 5.7%. For $C_{2n}H_{2n+2}$, where $n = 4$–8, there are ab initio results using STO-3G, 6-31G, 6-31G* and 6-31G + pd basis sets [2]. The MNDO results are in very good agreement with those produced with the 6-31G + pd set (Tables 1, 3). The remarkable success of MNDO for the computation of the polarizability values is due to an additional correction [21]. This parameter corrects to a considerable extent the error due to the underestimation of the atomic polarizabilites. With this correction we observe:

$$\alpha(\mathrm{MNDO}) > \alpha(\mathrm{PM3}) \ .$$

It is also found that for $C_{2n}H_{2n+2}$:

$$\gamma(\mathrm{MNDO}) > \gamma(\mathrm{PM3}) \ .$$

The difference in the γ values obtained by the two methods is not large.

Comparing the MNDO computed values for γ of $C_{2n}H_{2n+2}$ with the experimentally determined ones, we observe that the ratio γ (exp.)/γ (theor.) for C_2H_4, C_4H_6 and C_6H_8 is −53.1, 6.4 and 3.0, respectively. Thus the quality of the computed γ values improves as n increases. Comparison of the MNDO results for γ with those produced using the 6-31G+pd [2] shows that for C_4H_6 the difference is 71.3%, while for $C_{2n}H_{2n+2}$, $n = 3$–8, the average difference is 29.9%. For $n \geq 8$, we observe that

$$\gamma(\mathrm{MNDO}) > \gamma(\text{6-31G}) \ .$$

This inequality in connection with the experimental results for $n = 1$–3 (Table 2) suggests that the MNDO γ values are likely to have a smaller discrepancy with the experimental data than the ab initio ones (6-31G). Satisfactory γ values are also obtained for $C_{2n}H_{2n+2}$, $n = 1$–3 using the CHF-PT-EB-CNDO method [22]. The properties of **B** have been computed with PM3 only, because the MNDO optimization failed to produce the correct structure. The MNDO has been used for **C** and **D**, while for **E**, which has been found to have the more promising nonlinear properties, all three methods, MNDO, PM3 and MNDO/d have been employed (Tables 3, 4).

The main trends emerging from the analysis of the polarizabilities and hyperpolarizabilities of the considered oligomers (Tables 3, 4) can be summarized by defining the ratios:

$$R_\alpha = \alpha(\mathbf{X})/\alpha(\mathbf{A}) \quad \text{and}$$

$$R_\gamma = \gamma(\mathbf{X})/\gamma(\mathbf{A}) \ ,$$

where the structures for **X**(**B**, **C**, **D** or **E**) and **A** are given in Fig. 1. The same method has been used to determine both the numerator and the denominator of the ratios (Table 5). Thus for R_α and $R\gamma$, which correspond to **C** and **D**, the MNDO method has been used; for **B** property values computed by PM3 have been employed and for **E** two ratios for each compound are presented, the first of which has been determined using MNDO and the second by MNDO/d.

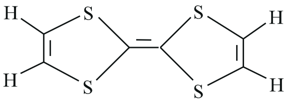
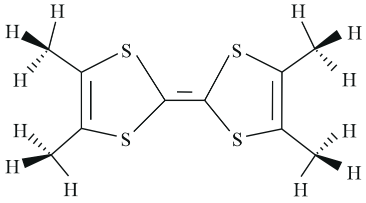
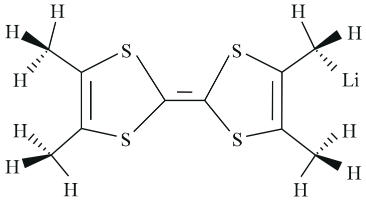
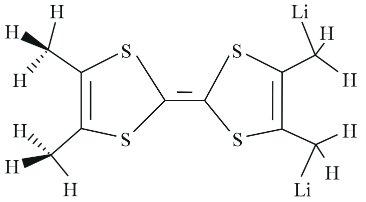
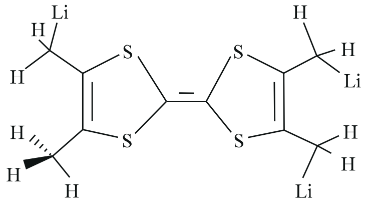
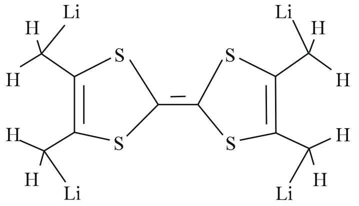
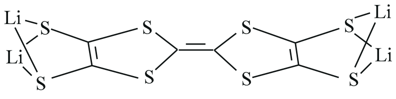
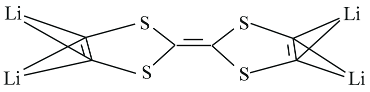
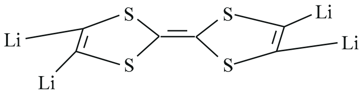
We observe (Table 5) that:

$$0.98 \leq R_\alpha \leq 2.87 \ ,$$

$$0.07 \leq R_\gamma \leq 5.14 \ .$$

It is also seen that R_α and R_γ increase with n (the number of double bonds) for the oligomers **B** and **E**. The reverse trend is observed for **C** and **D**. It is shown that $\gamma(\mathbf{B}) >$

Table 9. The effect of lithiation of TTF and some of its derivatives, on α and γ determined by MNDO(I), PM3(II) and MNDO/d(III)

	Molecule	α/a.u.	$\gamma \times 10^{-4}$/a.u.
1		119(I) 111(II) 128(III)	1.67(I) 2.03(II) 3.44(III)
2		180(I) 148(II) 172(III)	3.06(I) 3.53(II) 5.70(III)
3		195(I) 172(II) 190(III)	5.95(I) 17.6(II) 9.31(III)
4		207(I) 207(II) 205(III)	10.7(I) 31.9(II) 10.5(III)
5		217(I) 236(II) 216(III)	12.0(I) 56.9(II) 13.1(III)
6		237(I) 273(II) 240(III)	19.1(I) 75.0(II) 16.3(III)
7		206(I) 254(II) 251(III)	12.7(I) 56.2(II) 17.2(III)
8		167(I) 200(II) 185(III)	11.6(I) 30.9(II) 16.9(III)
9		169(I) 214(II) 191(III)	13.3(I) 53.3(II) 13.5(III)

$\gamma(\mathbf{A})$ for n = 13, and $\gamma(\mathbf{E}) > \gamma(\mathbf{A})$ for n ≥ 8 (MNDO). However, if MNDO/d is used the oligomer **E** is more polarizable than **A** even for n ≥ 4.

Thus the main finding of this section is that oligomers **E** have very polarizable structures indeed.

3. 3 Effect of lithiation on α and γ

Lithiated derivatives have been the subject of many studies, primarily to find their structures, which are often rather unusual. In this work compounds including lithium are of interest, because Li is known to be a very polarizable element. The polarizability and, in particular, the second hyperpolarizability of Li_2 are extremely large ($\alpha = 204$ and $\gamma = (910 \pm 50) \times 10^3$ a.u. [7]). The α and γ values of H-H are 5.192 and 609 a.u., respectively [23], while substitution of a hydrogen atom by lithium gives Li-H, which has $\alpha = 27.15 \pm 0.05$ and $\gamma = (90.7 \pm 5.6) \times 10^3$ a.u. [11e]. The γ values of both LiH and Li_2 are much larger than that of C_6H_6 (benzene: 11,710 ± 1,443 a.u. [24]). Taking these data into account we thought that it would be interesting to investigate the effect of changes induced on the polarizability and second hyperpolarizability by lithiation. Thus we replaced H by Li in C_2H_4 (ethylene), C_6H_6 (benzene), $C_6S_4H_4$ (TTF) and the classes of oligomers **B** and **E** (Fig. 1).

The geometries (bond length and angles) used for the computation of the properties (α, γ) have been optimized employing the semi-empirical method with which α and γ are calculated. For C_2H_4 and C_6H_6 both computed and experimental geometries have been used. The α and γ values, calculated with the experimental and theoretical geometries, are in good agreement (Table 7).

From the PM3 results of Table 7 we observe that:

$$\alpha(C_2Li_4)/\alpha(C_2H_4) = 12.5 \ ,$$

$$\gamma(C_2Li_4)/\gamma(C_2H_4) = 1.6 \times 10^4 \ .$$

The quite large effect of lithiation on the second hyperpolarizability is clearly seen. The polarizability is affected remarkably but to a less extent. A similar trend is also shown by the MNDO results. Computational studies on C_2Li_4 have been reported by Nagase and Morokuma [25a] as well as by Dorigo et al. [25b].

The synthesis of hexalithiobenzene has been reported by Baran et al. [25c] and computational studies on its structure have been performed by Xie and Schaefer [26a] and Smith [26b]. In the first study [26a] a basis set approaching triple-zeta plus polarization (TZP) quality was used, at the SCF level. They also noted that C_6Li_6 may be considered as "aromatic" and they supported this by using the C-C bond distance they found (1.415Å; TZP SCF) as well as the electron configuration [26a]. Smith [26b] determined a structure for C_6Li_6, using various theoretical models (SCF/TZP, MP2/TZP, etc.), which is lower in energy than that of Xie and Schaefer and which "can be described as a tightly clustered trimer of C_2Li_2 units".

We have computed α and γ of C_6Li_6, using three sets of geometries. The first structure is of D_{6h} symmetry, suggested by Xie and Schaefer [26a], and optimized with MNDO and PM3. Comparing the polarizabilities and hyperpolarizabilities of C_6H_6 and C_6Li_6, we observe (PM3; Table 7):

$$\alpha(C_6Li_6)/\alpha(C_6H_6) = 5.09 \ ,$$

$$\gamma(C_6Li_6/\gamma(C_6H_6) = 7.2 \times 10^2 \ .$$

Thus lithiation of C_6H_6 led to a very large increase in the second hyperpolarizability value of the resulting derivative.

The second set of computations was performed using the ab initio SCF/TZP bond lengths and angles (D_{6h}) given in Ref. [26a]. There is a reasonable agreement between the MNDO optimized and the SCF/TZP geometric data [26c] and thus both sets of α and γ values are in good agreement (Table 7). The PM3 and the SCF/TZP structures are in fair agreement [26c]. However, the PM3 optimized R(C-Li) and R(Li-Li) are a little larger than those given by SCF/TZP [26c]. This small difference in the above lengths leads to a noticeable discrepancy in the α and γ values computed with the PM3 method and using the ab initio SCF/TZP and PM3 geometries (Table 7). This interesting feature has been confirmed by ab initio SCF/STO-3G*+ [26d, 27a] computations for C_6Li_6 (D_{6h}). The polarizabilities are 213 a.u. and 236 a.u. for the SCF/DZP and PM3 optimized geometries, respectively. The corresponding second hyperpolarizabilities are 703×10^3 and 113×10^4 a.u.

The third set involved the ab initio SCF/TZP structure reported by Smith [26b]. We observe that this geometry is associated with remarkably lower α and γ values than those derived using the D_{6h} symmetry.

Now we proceed to study the properties of the lithiated derivatives of **B** and **E**, which are produced by substituting the four terminal hydrogen atoms (two on each side) by lithium. Lithiation of oligomer **B** (Fig. 1) has a considerable effect on α and even more on γ. The lithiated oligomers **(E)** however, show really exceptional features (Table 8). Thus for derivatives having four conjugated double bonds we observe:

$$\gamma(\mathbf{E})/\gamma(\mathbf{A}) = 98.6 \ .$$

Lithiated oligomer **E** with 12 conjugated double bonds has $\gamma \approx 4 \times 10^7$ a.u., which is extremely large. It is 12 times larger than the second hyperpolarizability of the corresponding hydrocarbon.

The properties of the lithiated TTF derivatives have been computed by using MNDO, MNDO/d and PM3. First we considered the derivative resulting by substitution of the four H atoms of TTF by CH_3 groups. This leads to the following changes in α and γ (MNDO/d; Table 9):

$$\alpha(\mathbf{2})/\alpha(\mathbf{1}) = 1.3, \quad \gamma(\mathbf{2})/\gamma(\mathbf{1}) = 1.7 \ .$$

The corresponding ratios using MNDO are 1.5 and 1.8. Progressive substitution of the four CH_3 groups by CH_2Li gives structures **3–6** (Table 9). These changes in structure are associated with a considerable increase in the second hyperpolarizability, having as reference the γ value of TTF. For example, using the PM3 values we observe:

$\gamma(\mathbf{6})/\gamma(\mathbf{1}) = 37$.

Substitution of the four H of TTF by SLi gives structure **7** (Table 9). The γ value of this derivative is 27 times larger than that of structure **1** (PM3). We also consider the lithiated derivatives of TTF (structure **1**), in which the four hydrogen atoms have been replaced by lithium atoms. The synthesis of this derivatives has already been reported [27b]. The structures **8** and **9** resulted after optimization. The former has lower energy than the latter using MNDO, but with PM3 and MNDO/d the reverse trend is observed. The polarizability values of structures **8** and **9** do not differ greatly, but their hyperpolarizability values show a remarkable difference (Table 9, PM3). As one would expect, SLi leads to a more polarizable structure than Li. However, comparing the functional groups CH_2Li and SLi, we note that the former leads to more polarizable derivatives (PM3):

$\alpha(\mathbf{6}) > \alpha(\mathbf{7})$,

$\gamma(\mathbf{6}) > \gamma(\mathbf{7})$.

Summarizing the above discussion we note that lithiation of TTF and some of its derivatives induced a large change in the second hyperpolarizability. This observation has been confirmed by three methods: MNDO, PM3 and MNDO/d.

We are not aware of any other semi-empirical work which reports polarizabilities or hyperpolarizabilities of organolithium derivatives. However, there are some ab initio computations, at the MP2 level, on the polarizabilities and hyperpolarizabilities of C_8H_6 and $C_8H_6Li_2$ [27c]. These calculations have been performed using the 6-31G** basis set, supplemented with diffuse functions. It has been shown that [27c]:

$\gamma(C_8H_6Li_2)/\gamma(C_8H_6) = 4.18$ . .

The above ratio confirms the present finding (which relies on a relatively large number of molecules) that lithiation may lead to a considerable enhancement of the molecular second hyperpolarizability.

The study of the carbon-lithium bond is an interesting and controversial issue [27d]. It would be rather inappropriate, though, to perform a Mulliken's population analysis using a semi-empirical method like the ones used in this work, due to the inadequacy of the basis set employed [27d,e]. However, Streitweiser et al. [27d] noted that "the carbon-lithium bond in theory and in chemical properties can be modeled as an essentially ionic bond.", and that "the relative energies of a number of organolithium compounds parallel those of the corresponding carbanions". It has been shown that the anions may have very large hyperpolarizabilities, which at any rate are larger than those of the corresponding neutral precursors [28]. Thus a combination of these observations allows us to rationalize the computed, enhanced hyperpolarizabilities of the lithiated derivatives. Finally, one should note that the present computations can only be used to model certain aspects of the behaviour of isolated molecules in uniform electric fields. Thus problems related to the solid state are beyond the scope of the present work.

4 Synopsis and conclusions

Several semi-empirical techniques (MNDO, PM3 and MNDO/d) have been used for the investigation of the structure-polarization relationship and for the selection or design of derivatives with very large second hyperpolarizability, γ. The studied compounds involved H, Li, C and S. Of primary importance for the present work are trends and differences, and their validity is safeguarded, to a great extent, by the considered variety of methods. In particular it is noted that the polarizabilities and hyperpolarizabilities of polyenes and other related compounds have been studied in the past, using methods that are similar to or the same as those employed in the present work. These authors have found reasonable property values, which in addition can promote our understanding of the nonlinear optical processes (e.g. Refs. [6b, 9a, 13, 15, 29]). Specifically, the MNDO model, in its usual (MNDO, PM3) and the extended version (MNDO/d), provides a consistent and adequate theoretical framework for the comparative and systematic study of the relatively large number of compounds considered here. The main findings of the present work are:

1. The quality of the computed hyperpolarizability values improves as the size of the molecule increases. In addition, although there are discrepancies between the polarizability and, in particular, the second hyperpolarizability values determined by the employed semiempirical models, the trends of interest are clearly shown by all models.
2. Two classes of compounds, that contain a conjugated backbone (Table 4**B** and **E**), have been found to have very large second hyperpolarizabilities, larger than the corresponding polyenes with the same number of double bonds.
3. A relatively large number of lithiated derivatives have been considered in this work. Some of these have already been synthesized (e.g. haxalithiobenzene [25c], tetralithio-TTF [27b]). The functional groups that have been employed and which involve lithium are commonly used in lithium chemistry: -CH_2Li [30], -Sli [30], -Li_2C = [27d] and -$Li_2CR_1R_2$ [27d]. There are also several articles which deal with various aspects (e.g. the structure) of some of the lithiated derivatives (e.g. C_6Li_6 [26a,b], C_2Li_4 [25a,b 27d]) studied here. Studies of the stability (e.g. to moisture) of organolithium compounds have shown that derivatives having lithium bonded to carbon are, in general, unstable, but those in which Li is bonded to S are much more stable [30]. It has been documented that Li as a substituent may lead to extremely large second hyperpolarizabilities (e.g. compare the properties of the pairs C_2Li_4/C_2H_4 and C_6Li_6/C_6H_6). This finding has been supported by the properties of a large number of compounds [27c].

For completeness it should be noted that after recognizing that a certain class of materials has interesting properties for some applications, there are many other problems to be considered and solved (e.g. those related to the production techniques and the construction of the actual device [31]).

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   1 a.u. of polarizability
   $\sim 0.148176 \times 10^{-24}$ esu
   $\sim 0.164867 \times 10^{-40}$ C^2 m^2 J^-
   1 a.u. of second
   hyperpolarizability $\sim 0.503717 \times 10^{-39}$ esu
   $\sim 0.623597 \times 10^{-64}$ C^4 m^4 J^{-3}

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   MNDO: R(C-C) = 1.463 Å
   R(Li-Li) = 3.011 Å
   R(C-Li) = 1.891 Å
   PM3: R(C-C) = 1.415 Å
   R(Li-Li) = 3.101 Å
   R(C-Li) = 2.004 Å
   SCF/TZP [26a] R(C-C) = 1.415 Å
   R(Li-Li) = 3.018 Å
   R(C-Li) = 1.927 Å

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