Non-linear Optical Properties of Organic Molecules. Part 2.† Effect of Conjugation Length and Molecular Volume on the Calculated Hyperpolarisabilities of Polyphenyls and Polyenes

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The calculated hyperpolarisabilities of the symmetrical polyphenyls, containing an electron-donating dimethylamino group and an electron-attracting nitro group positioned at opposite ends of the conjugated system, slowly increase with an increasing number of phenyl units, but the effect per unit volume is a maximum for 4-dimethylamino-4′-nitroterphenyl. In contrast, the calculated values for polyenes containing the same donor and attractor increase rapidly with an increasing number of ethenyl units, and the effect per unit volume is a maximum for 20 units. Overall, the polyene system shows an effect which is at least 20 times that of the polyphenyl system and 10 times that of any other known system. A similar effect is also found in the dimethylaminopolyenals, though a comparison between calculated and experimental dipole moments and electronic transition energies suggests that their hyperpolarisabilities may be somewhat overestimated at the CNDO level of approximation.

A considerable effort is now underway to exploit the non-linear optical properties of organic molecules in a variety of electro-optic devices.[1] Conjugated organic systems show a very large optical response in an external field (E) which can be expressed in terms of equation (1) where u_i is the ith component of the

$$u_i(\text{ind}) = u_i - u_{oi} = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \ldots \quad (1)$$

induced dipole, u_i and u_{oi} refer to the perturbed and unperturbed ground-state dipoles, respectively, and α, β, and γ are the first-, second-, and third-order polarisability tensors, respectively.

We have recently reported calculations on the second-order polarisability or hyperpolarisability (β_{ijk}) of an extended set of organic molecules using a version of the CNDO/S method,[2] and shown good correlations with experimental data obtained from Electric Field Induced Second Harmonic Generation (EFISH) in solution.[1] The present studies are concerned with a systematic investigation of the effect of conjugation on the calculated hyperpolarisability (β_x) of a series of extended polyphenyls and polyenes containing appropriate electron donors and attractors positioned at either end of the chain. It has been established empirically that an extension of the conjugation path between appropriate substituents results in a substantial increase in the value. For example, 4-amino-4′-nitro-*trans*-stilbene has a molecular effect which is at least 10 times that of 4-nitroaniline.[3] However, the overall effect in terms of non-linear optical efficiency is substantially less than this factor would suggest because fewer molecules of the stilbene can pack in a given volume of crystal and the observed effect per unit volume is much reduced. Consequently an attempt has been made in this work to evaluate the hyperpolarisability per unit volume or hyperpolarisability density, ρ, where $\rho = \beta_x/V$ where V is expressed simply as Å^3 (10^{-30} m^3).

$$\begin{aligned}\beta_{ijk}^{2\omega} + \beta_{ikj}^{2\omega} &= (-e^3/4\hbar^2) \\ \times \sum_{n'}\sum_{n} \Bigg\{ &({r^j}_{gn'}{r^i}_{n'n}{r^k}_{ng} + {r^k}_{gn'}{r^i}_{n'n}{r^j}_{ng}) \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} - \omega)}\right] + \\ &({r^i}_{gn'}{r^j}_{n'n}{r^k}_{ng} + {r^i}_{gn'}{r^k}_{n'n}{r^j}_{ng}) \left[\frac{1}{(\omega_{n'g} + 2\omega)(\omega_{ng} + \omega)} + \frac{1}{(\omega_{n'g} - 2\omega)(\omega_{ng} - \omega)}\right] + \\ &({r^j}_{gn'}{r^k}_{n'n}{r^i}_{ng} + {r^k}_{gn'}{r^j}_{n'n}{r^i}_{ng}) \left[\frac{1}{(\omega_{n'g} - \omega)(\omega_{ng} - 2\omega)} + \frac{1}{(\omega_{n'g} + \omega)(\omega_{ng} + \omega)}\right]\Bigg\} \quad (2)\end{aligned}$$

$${r^i}_{gn} = <\psi_g| \sum_{m=1}^{n} r^i(m)|\psi_n> \text{ or } <g|r^i|n> \quad (3)$$

All calculations reported here were carried out with the CNDOVSB method[2] which involves an initial configuration interaction treatment of ground (g) and excited state (n and n') wave functions and then evaluation of the hyperpolarisability tensor from the improved wave functions using expression (2).[4] Here ${r^i}_{gn}$ is defined by expression (3) where $r^i(m)$ is the ith component of the position vector of electron m (of N), ${r^i}_{n'n} = <n'|r^i|n>$, ω_{ng} is the eigenvalue of ψ_n, relative to the ground-state ψ_g (the electronic transition energy), e is the magnitude of the electronic charge, and ω is the frequency of the applied radiation field. All components of the tensor are calculated, but the most relevant quantity, which relates to the experimental data from EFISH measurements, is the vector component, β_x, defined by equation (4) where x is aligned along the direction of

$$\beta_x = \beta_{xxx} + \tfrac{1}{3}\Sigma\,(\beta_{xii} + 2\beta_{iix}) \quad (4)$$

the dipole moment, and y lies in the molecular plane. Because the absorption frequency (ω_{ng}) of many conjugated molecules coincides with the second harmonic (2ω) of the applied field of

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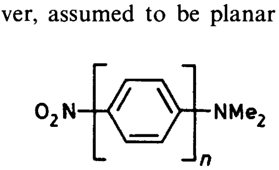
† Part 1, Ref. 2.

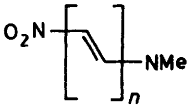
fundamental frequency, ω, the calculated value of β_x tends to infinity through terms in the denominator of equation (2): consequently calculations are reported here both at ω = 0 (an applied field of zero frequency) and also at a suitable frequency, ω, such that 2ω is well removed from ω_{ng}.

The polyphenyls and polyenes (**I**)—(**III**) selected for calculation were constructed from molecular fragments which were manipulated on a calligraphic screen display using a molecular graphics program and substituted with the *NN*-dimethylamino group at one end of the molecule and either the nitro or formyl group at the other to represent examples of both powerful electron donors and acceptors. Calculations were carried out directly from the graphical display by submission of atomic numbers and cartesian co-ordinates to the molecular orbital program mounted on an IBM 3083 series computer.

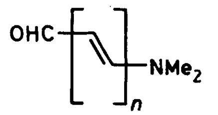
Molecular Templates.—An examination of the Cambridge database[5] shows many examples of bi-, ter-, and quaterphenyls. For simple structures, the molecules are generally planar with the Ar–Ar bond distance in the range 1.47—1.51 Å though substituted derivatives containing polar groups tend to be non-planar (Table 1). The polyphenyl test molecules (with *n* 1—9) were, however, assumed to be planar in the molecular state and constructed from standard benzene rings with C–C and C–H bond lengths of 1.40 and 1.08 Å, respectively, and with central Ar–Ar bond lengths of 1.49 Å. The substituent geometries adopted for each member of the series and shown for 4-(*NN*-dimethylamino)-4′-nitrobiphenyl (**Ia**) are derived from the crystal structure of *NN*-dimethyl-4-nitroaniline[6] although the Ar–NO_2 distance is considerably shorter than that found in most substituted nitroarenes.



(I)



(II)



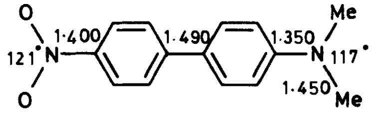
(III)

Table 1. Crystal-structure data on representative polyphenyls from the Cambridge database[5]

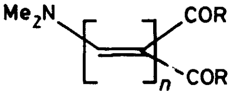
Molecule	Substituents	Ar–Ar distance (Å)	Torsion angle (°)[a]	Cambridge reference[b]
Biphenyl	None	1.5074	PL	BIPHEN
	None	1.5074	PL	BIPHEN01
	None	1.4956	PL	BIPHEN02
	None	1.4926	PL	BIPHEN04
	4-NO_2	1.4785	29	NBPHEN
	2-NO_2,4′-NH_2	1.4737	57	NIAMBP
	2-NO_2,4′-$COCH_3$	1.4855	46	ACNTBP
	4,4-$(NH_2)_2$ 3,3-Cl_2	1.5147	21	ACLBPH
	$^2H_{10}$	1.4949	10	DDBIPH
	$^2H_{10}$	1.4949	PL	DDBIPH01
Terphenyl	$^2H_{14}$	1.4692	PL	DEUTPH
	None	1.4978	PL	TERPHE01
	None	1.4950	PL	TERPHE02
	None	1.4766	PL	TERPHE03
	None	1.5030	PL	TERPHE04
	None	1.5030	PL	TERPHE06
Quater-phenyl	None	1.4860	PL	QUPHEN
		1.5023	PL	
	None	1.4984	20	QUIPHEN01
		1.5001	20	

[a] Of one ring relative to the other, PL implies a planar structure with torsion angles between adjacent rings < 3°. [b] The codenames are unique and taken from ref. 5.

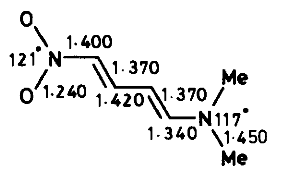
The structures of the polyenes have been derived from crystallographic data on related systems such as dimethyl *trans*-1-(*NN*-dimethylamino)hexa-1,3,5-triene-6,6-dicarboxylate (**IV**; *n* = 3) and 3-acetyl-6-(*NN*-dimethylamino)hexa-3,5-dien-2-one (**V**; *n* = 2).



(Ia)



(IV) R = OCH_3
(V) R = CH_3



(IIa)

In these structures (*n* 2—5) the alternating single bonds vary from 1.40 to 1.44 Å while the double bonds vary from 1.35 to 1.38 Å (Table 2). The aminonitropolyenes (**II**) were constructed from a standard butadiene template derived from the experimental data with all angles set at 120° except those specified below. The substituent geometries are taken from the well resolved crystal structure of *NN*-dimethyl-2-nitroethenamine[7] and the geometry of a typical example of this series, 1-(*NN*-dimethyl)-4-*trans*-nitrobuta-1,3-diene (**IIa**), is illustrated.

The same geometry was adopted for the aminopolyenals (**III**) with the nitro group replaced by a formyl group. The geometry of the latter is taken from the crystal structure of 5-(*N*-methyl-α-naphthylamino)penta-2,4-dienal[8] with C=O and C=C bond lengths of 1.2214 and 1.4250 Å, respectively.

Results and Discussion

(1) *Polyphenyls*.—The calculated β_x value (expressed throughout in units of 10^{-30} cm^5 e.s.u.$^{-1}$) of the polyphenyls (**I**) increases with an increase in the number (*n*) of aromatic rings present between the electron-attracting nitro group and the electron-donating dimethylamino group both at zero frequency (ω 0) and at an applied frequency of 1.17 eV as expected (Table 3). However, as the series is ascended the number of π-electrons increases and an increasing number of excited states is required in the calculation before the β_x value smoothly converges to an optimum value. Thus for earlier members of the series (*n* 1—3), 50 included states are sufficient, for intermediate members (*n* 4—6) 100 included states are required, and for large molecules (*n* 7—9) up to 200 included states are necessary before oscillations in the β_x value largely disappear. This effect is illustrated for 4-dimethylamino-4′-nitroseptiphenyl where the wide oscillations obtained in the calculated value for < 100 states gradually diminish as more states are included in the calculation (Figure 1). Although β_x is still rising with an increase in the number of rings at *n* 6, the hyperpolarisability per unit volume, ρ, shows that the optimum value is obtained for the

Table 2. Bond length data on representative polyenes from the Cambridge database[5]

Bond type[b] (Å)	Cambridge reference[a]						
	MXCABD10	MAMHCA	CEYJOF	CILHEK	ACHXDO	BPZHTR	DPHOCE
N(1)–C(2)	1.339	1.329	1.345	1.346	1.322		
C(2)=C(3)	1.359	1.371	1.349	1.365	1.378	1.381	1.334
C(3)–C(4)	1.408	1.395	1.406	1.441	1.405	1.437	1.442
C(4)=C(5)	1.376	1.373	1.375	1.368	1.395	1.348	1.337
C(5)–C(6)		1.404	1.400	1.441		1.420	1.445
C(6)=C(7)		1.370	1.354	1.366		1.356	1.337
C(7)–C(8)			1.398	1.431			1.442
C(8)=C(9)			1.386	1.382			1.334
C(9)–C(10)				1.430			
C(10)=C(11)				1.380			
R^1	NMe_2	NMe_2	NMe_2	NMe_2	NMe_2	C_6H_4Br	C_6H_5
R^2	CO_2Me	CO_2Me	CO_2Me	CO_2Me	COMe	COC_6H_5	C_6H_5
R^3	CO_2Me	CO_2Me	CO_2Me	CO_2Me	COMe	H	H

[a] Defined in Table 1. [b] The numbering convention is as follows:

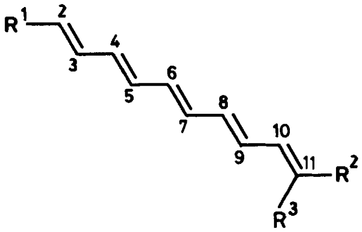


Table 3. Calculated hyperpolarisabilities,[a] dipole moments, and spectroscopic data for polyphenyls (I)[b]

n	Dipole moment (D)		Transition energy (nm)	Oscillator strength	β_x (ω 0)	β_x (ω 1.17 eV)	Volume (Å^3)
	Ground state	Excited state					
1	9.03	18.22	331.6	0.64	12.29	24.56	145.7
2	9.72	24.02	373.9	0.97	31.35	83.91	214.8
3	9.97	26.05	387.0	1.33	42.17	130.47	285.3
4	10.13	25.15	391.4	1.76	47.74	155.45	354.1
5	10.19	22.98	393.1	2.21	49.36	163.81	423.8
6	10.23	20.89	395.3	2.68	52.95	176.30	493.3
7	10.25	19.39	396.0	3.13	53.00	180.21	561.5
8	10.33	18.19	396.9	3.60	54.07	182.86	630.9
9	10.34	17.09	397.6	4.08	53.51	179.17	699.1

[a] In units of 10^{-30} cm^5 e.s.u.$^{-1}$. [b] Using 150 included states in the calculation for *n* 1—5, and 200 thereafter.

Table 4. Calculated hyperpolarisabilities,[a] dipole moments, and spectroscopic data for polyenes (II)[b]

n	Dipole moment (D)		Transition energy (nm)	Oscillator strength	β_x (ω 0)	β_x (ω 0.656 eV)	Volume (Å^3)
	Ground state	Excited state					
2	11.94	16.66	389.5	1.07	14.80	19.49	130.8
4	15.47	22.34	507.9	1.99	80.58	133.89	183.0
6	17.95	27.16	603.3	2.79	237.8	520.0	241.4
8	19.78	30.78	679.4	3.53	491.8	1 445.2	292.5
10	21.14	33.38	740.4	4.22	827.0	3 307.7	346.3
12	22.54	34.96	793.3	4.95	1 211.4	6 809.8	402.3
14	23.38	35.73	832.7	5.61	1 566.0	12 413.1	457.3
16	24.03	35.99	863.9	6.27	1 888.4	21 475.3	509.3
18	24.57	36.18	889.6	6.91	2 238.3	38 066.6	562.0
20	24.97	35.86	909.5	7.55	2 468.2	66 960.1	616.5
22	25.27	35.41	925.3	8.20	2 659.4	132 104.4	670.5
24	25.52	35.22	929.4	8.20	2 823.5	175 409.0	724.00

[a] In units of 10^{-30} cm^5 e.s.u.$^{-1}$. [b] Using 100 included states in the calculation throughout.

terphenyl (**I**; $n = 3$) as illustrated (Figure 2); thereafter there is a decreasing return as additional rings are added to the system. A comparison between the calculated and experimental data where available shows the usual overestimation in the ground-state dipole moments, (9.03 *versus* 6.84 D for *n* 1, and 9.72 *versus* 6.93 D for *n* 2),[9] and underestimation in the electronic transition energies (331 *versus* 351 nm for *n* 1, and 374 *versus* 398 nm for *n* 2)[10] which is a consequence of the parameterisation scheme adopted in the CNDOVSB method.[2]

(2) *Polyenes*.—(a) *Aminonitropolyenes* (**II**). β_x Values of the aminonitropolyenes (**II**) were calculated both at zero frequency (ω 0) as before and at an applied frequency in this series of 0.656 eV (1 890 nm) to ensure that the absorption frequency of each molecule, which was expected to lie in the range 500—800 nm, was well removed from the second harmonic frequency of the applied field (945 nm). The results show that the β_x values increase sharply with an increase in the number (*n*) of vinyl units between the electron attractor and donor (Table 4). Unlike the polyphenyls, however, the effective hyperpolarisability density ρ increases with increasing chain length up to *n* 20 at which point it begins to level out (Figure 3). Indeed, the optimum value

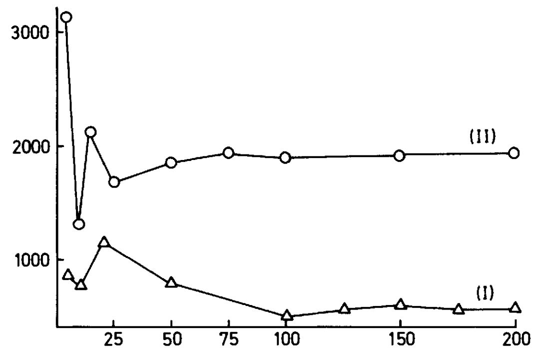


Figure 1. Effect of the number of included states (*N*) on the calculated hyperpolarisability ($\beta_x^{1\cdot 17}$in 10^{-30} cm^5 e.s.u.$^{-1}$) of polyphenyls (**I**) (actual values × 10) and polyenes (**II**) (actual values)

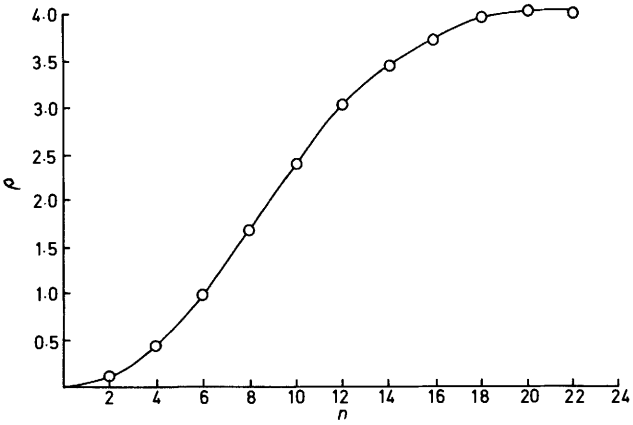


Figure 3. Effect of increasing chain length (*n*) on the calculated hyperpolarisability density (ρ) of polyenes (**II**)

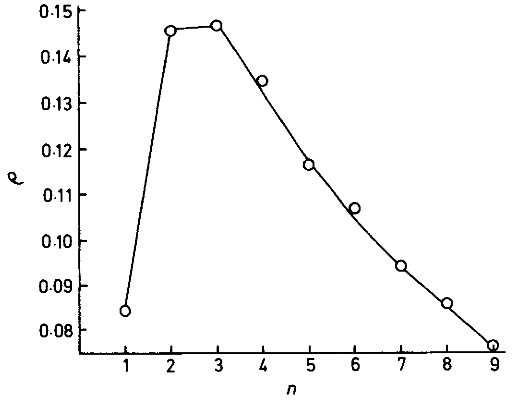


Figure 2. Effect of increasing chain length (*n*) on the calculated hyperpolarisability density (ρ) of polyphenyls (**I**)

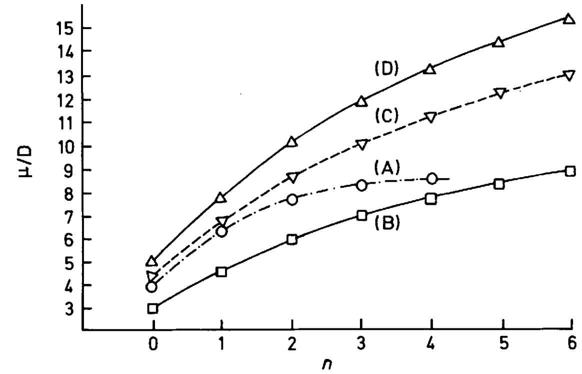


Figure 4. Effect of increasing chain length (*n*) on the dipole moment (μ) of the polyenals (**III**): (A) experimental; (B) STO-3G; (C) 3-21G; (D) CNDOVSB

Table 5. Calculated hyperpolarisabilities,[a] dipole moments, and spectroscopic data for polyenals (**III**)[b]

	Dipole moment (D)						
n	Ground state	Excited state	Transition energy (nm)	Oscillator strength	β_x (ω 0)	β_x (ω 0.656 eV)	Volume (Å^3)
0	4.95	9.14	210.4	0.32	0.28	0.33	73.9
1	7.66	10.51	294.9	0.74	2.90	3.42	101.1
2	10.05	13.16	375.4	1.22	9.96	12.91	128.3
3	11.76	16.08	439.9	1.66	27.44	39.85	154.3
4	13.10	18.62	496.3	2.08	59.94	98.35	179.0
5	14.26	20.93	546.6	2.48	110.85	207.41	211.3
6	15.17	22.80	591.2	2.86	180.13	386.26	235.3

[a] In units of 10^{-30} cm^5 e.s.u.$^{-1}$. [b] Using 50 included states in the calculation.

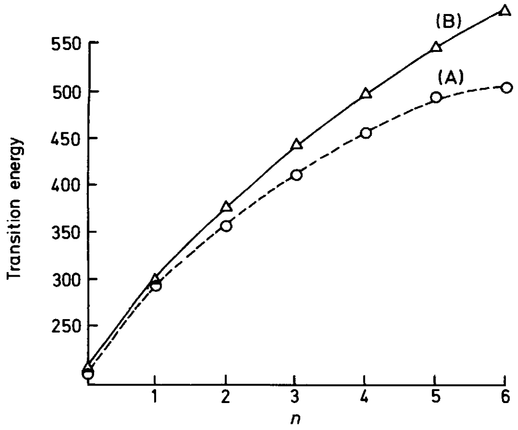


Figure 5. Effect of increasing chain length (n) on the calculated transition energies (nm) of the polyenals (**III**): (A) experimental; (B) CNDOVSB

obtained from the polyphenyls (**I**; $n = 3$) is rapidly reached and soon surpassed by the polyenes even at short chain length. The overall β_x value for these molecules exceed those for the best known experimental molecules such as 4-*NN*-dimethylamino-β-nitrostyrene, 4-*NN*-dimethylamino-4′-nitrostilbene, and 1-(4-*NN*-dimethylaminophenyl)-4-buta-1,3-diene.[3]

The effect of the number of states included on the calculated β_x value has been examined also for these systems, but in this case using from 5 to 100 states and taking the hexadecaoctaene (**II**; $n = 16$) as a typical example. As the number of states included in the calculation increases, the early oscillation in the β_x value disappears to be replaced by a smooth convergence to an optimum value obtained using 100 states (Figure 1).

A comparison between the theoretical and experimental results is not possible in these cases since data are only currently available on *NN*-dimethyl-2-nitroethenamine (**II**; $n = 1$). However, both the dipole moment and electronic transition energy rise sharply for n 3—10 but thereafter the values begin to level off in accord with results on related systems (see below). Although the β_x values obtained for the polyenes at $n > 8$ are considerably higher than any other system currently explored either theoretically or experimentally, the electronic transition energies also rise with increasing values of n, and for n 24 the transition energy (929 nm) and the second harmonic (945 nm) are almost resonant. It follows that the large β_x values calculated can only be realised for applied fields of lower energy for frequency doubling applications, though it is clear that the materials are useful for other applications such as the Pockels effect.[1,3]

(b) *Aminopolyenals* (**III**). Calculations on this series (Table 5) show similar trends to the previous cases, and the β_x and ρ value increase with increasing values of n, though the formyl group is less effective as an electron acceptor. However, because all of these molecules are known, along with their dipole moments[11] and electronic absorption spectra,[12] a comparison can be made between the calculated and experimental data.

The correlation between the calculated and experimental dipole moments is only satisfactory for $n \leqslant 3$, thereafter the values diverge rapidly as the experimental value levels out (Figure 4). Because this discrepancy casts doubt on the calculated results obtained not only in this series but also in the aminonitropolyenes, further calculations have been carried out at the *ab initio* level using the same geometries as those used for the CNDOVSB method.

The STO-3G method surprisingly underestimates the dipole moments by a substantial margin though the values obtained continue to rise smoothly with increasing values of n. In contrast, dipole moments calculated at the 3-21G level show an excellent correlation with the experimental data for early members of the series but again the calculated values rise as before in contrast to the experimental data (Figure 4). On the whole the results at the CNDOVSB level correlate with those at 3-21G level and it is concluded that the discrepancy observed between theory and experiment is either a result of the selection of poor geometries for the higher members of the polyenals ($n > 3$) or errors in the experimental measurements arising from the increasing insolubility as the series is ascended. Indeed, the dipole moment measurements could not be carried out on the series above $n > 4$ for this reason.

The correlation between the calculated and observed transition energies, however, is reasonably good up to $n \leqslant 4$, thereafter, the value begins to diverge (Figure 5) which may reflect again inaccurate geometries used in the calculation or errors in the experimental data arising from the presence of *cis* isomers rather than all-*trans* forms present for small values of n.

It is concluded that polyenes containing an electron donor at one end of the molecule and an electron attractor at the other have a much larger hyperpolarisability than the corresponding polyphenyls though there is a possiblity that the calculated values are overestimated at long chain lengths.

Acknowledgements

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