Nonlinear Optical Properties of Organic Molecules. Part 15.† Calculation of the Structure and Hyperpolarisabilities of Arylalkenes containing Weak Donors and Acceptors

John O. Morley
Chemistry Department, University College of Swansea, Singleton Park, Swansea, UK SA2 8PP

The structure of a series of 4-methoxyphenylpolyenals and furylpolyenals have been calculated at the AM1 level. The hyperpolarisabilities of these systems calculated using a semi-empirical sum-over-states approach increase with increasing conjugation path length between the aromatic ring and the terminal aldehyde group. The initial members of the series in both cases are transparent, possess relatively large hyperpolarisabilities which are comparable to molecules containing strong donors and acceptors, and have potential application as materials for second harmonic generation.

A considerable number of organic molecules have now been identified as effective materials for applications in nonlinear optics particularly for second harmonic generation (SHG) where there are a number of important applications in optical data storage. Here the low energy emission from a semiconductor laser is converted from the IR region at around 800 nm to the blue region at 400 nm enabling four times as much data to be written.[1-4] Active molecules for these applications must be transparent at the SHG wavelength to prevent reabsorption of the converted light, and possess a large molecular hyperpolarisability usually through the presence of a donor and acceptor group situated at either end of a suitable conjugation path.

Most theoretical studies on the nonlinear properties of conjugated organic molecules and their frequency dependent effects have been carried out by calculating their molecular hyperpolarisabilities using molecular orbital theory coupled with sum-over-states (SOS) procedures[5-10] based on a perturbation formalism derived by Ward[11] where the appropriate formula for the hyperpolarisability tensor (β_{ikj}) is given by eqn. (1);

$$\beta^{2\Omega}_{ijk} + \beta^{2\Omega}_{ikj} = (-e^3/4\hbar^2) \times \sum_{n'n} \tag{1}$$

$$[(r^j_{gn'}r^i_{n'n}r^k_{ng} + r^k_{gn'}r^i_{n'n}r^j_{nh})\{[(\Omega_{n'g} - \Omega)(\Omega_{ng} + \Omega)]^{-1} + [(\Omega_{n'g} + \Omega)(\Omega_{ng} - \Omega)]^{-1}\}$$

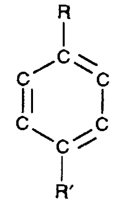
$$+ (r^i_{gn'}r^j_{n'n}r^k_{ng} + r^i_{gn'}r^k_{n'n}r^j_{ng})\{[(\Omega_{n'g} + 2\Omega)(\Omega_{ng} + \Omega)]^{-1} + [(\Omega_{n'g} - 2\Omega)(\Omega_{ng} - \Omega)]^{-1}\}$$

$$+ (r^j_{gn'}r^k_{n'n}r^i_{ng} + r^k_{gn'}r^j_{n'n}r^i_{ng})\{[(\Omega_{n'g} - \Omega)(\Omega_{ng} - 2\Omega)]^{-1} + [(\Omega_{n'g} + \Omega)(\Omega_{ng} + 2\Omega)]^{-1}\}]$$

where r_{gn} is defined as

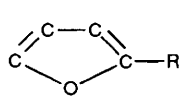
$$r_{gn} = \langle \varphi_g|\Sigma\, r^i(\mathrm{m})|\varphi_n\rangle \text{ or } \langle g|r^i|n\rangle$$

and r^i(m) is the ith component of the position vector of electron m (of N), $r_{nn} = \langle n|r^i|n\rangle$, Ω_{ng} is the eigenvalue of φ_n relative to the ground state φ_g (the electronic transition energy), e is the magnitude of the electronic charge, and Ω is the frequency of the applied radiation field. The indices n and n' may be restricted to run over excited states in increasing energy provided $\langle g|r|g\rangle = 0$ which holds only in the electronic charge centroid system as discussed previously.[7]



1

1a R = NH_2; R′ = NO_2
b R = NMe_2; R′ = NO_2
c R = OMe; R′ = NO_2
d R = NMe_2; R′ = CHO
e R = OMe; R′ = CHO
f R = OMe; R′ = [CH=CH]CHO
g R = OMe; R′ = $[CH=CH]_2CHO$
h R = OMe; R′ = $[CH=CH]_3CHO$
i R = OMe; R′ = $[CH=CH]_4CHO$



2

2a R = CHO
b R = [CH=CH]CHO
c R = $[CH=CH]_2CHO$
d R = $[CH=CH]_3CHO$
e R = $[CH=CH]_4CHO$

All 27 components of the SHG tensor are calculated using this expression but the most appropriate quantity is the vector component, β, theoretically defined in eqn. (2);[7] where

$$\beta = \beta_{\mu\mu\mu} + 1/3 \sum_{i\neq\mu} (\beta_{\mu ii} + \beta_{ii\mu}) \tag{2}$$

β is aligned to lie along the direction of the molecular dipole moment and is therefore directly related to the nonlinear coefficients derived both from electric field induced second harmonic generation in solution and in poled polymer films where molecules are orientated along the direction of their dipole moments by a strong DC field.[1,4]

The calculated hyperpolarisability of conjugated aromatic systems using the SOS approach has been shown to be derived mainly from π–π* electron transitions, and for substituted benzenes such as 4-nitroaniline (**1a**), a limited number of excited states contribute to most of its value.[5,6,9] The change in π-electron distribution in the aromatic ring on excitation for a given substituent has been used to derive a scale of ground and excited state substituent constants which have been related to their effective hyperpolarisability.[12] Substituents such as the nitro- and nitroso-groups are the strongest attractors while the dimethylamino-group is the strongest donor. However, if these groups are combined through an appropriate aromatic con-

---

† Part 14, see ref. 23.

Table 1 Experimental absorption spectra and dipole moments of donor–acceptor arenes (**1** and **2**)

Structure	λ^a	μ^b
1a	375	6.29
b	395	6.84
c	305	4.89
d	342	5.58
e	277	3.26
f	322	
g	352	
h	382	
i	403	
2a	276	3.58
b	312	
c	346	
d	366	
e	389	

^{a} Transition energy or absorption maximum (in nm) from ref. 13. ^{b} Dipole moment (in D) from ref. 14.

jugation path, as in *N,N*-dimethylamino-4-nitroaniline (**1b**), the resulting molecule cannot be used for second harmonic generation because in a concentrated medium such as a crystal or a polymer film, the tail of the charge transfer absorption band (351 nm in hexane and 395 in chloroform)[13] extends into the blue region of the spectrum. The introduction of weaker substituents in place of the strong donor and acceptor groups usually results in a beneficial hypsochromic shift towards the UV region.

Thus the replacement of the strong electron donating dimethylamino-group in *N,N*-dimethyl-4-nitroaniline (**1b**) by the weaker methoxy-group to give 4-nitroanisole (**1c**) results in a large hypsochromic shift in the absorption maximum. A similar shift occurs if the electron attracting nitro-group in the same molecule (**1b**) is replaced by the weaker aldehyde group to give 4-(*N,N*-dimethylamino)benzaldehyde (**1d**), and if both are replaced the resulting 4-methoxybenzaldehyde (**1e**) only absorbs in the UV region (Table 1).[13] Alternatively, simple heterocyclic systems with donor–acceptor properties could also be used as many absorb solely in the UV region, *e.g.* 2-furaldehyde (**2a**).[13]

However, the majority of these molecules show a marked reduction in the calculated hyperpolarisabilities with the introduction of weaker donor and acceptor groups to a level which is unacceptable for centrosymmetric materials which require additional functionality to induce order, such as the addition of large inactive hydrocarbon chains for Langmuir–Blodgett films or monomeric alkenyl units for polymerisation.[4] In addition to this dilution effect, the dipole moments decrease with the hypsochromic shift[14] and it is unlikely that the resulting molecules can be significantly orientated in poled polymer films.

Previous studies have shown that the hyperpolarisabilities of donor–acceptor polyenes[8,15] are substantially greater than those for simple aromatics though most systems of interest show strong absorption in the visible region of the spectrum. It would be expected that the hyperpolarisability of mixed systems containing weak donors and weak acceptors would be substantially greater than those of the simple aromatics themselves. The present studies have been carried out to probe the effect of inserting a series of alkene groups between the aromatic ring and a weak acceptor. Both 4-methoxybenzaldehyde (**1e**) and 2-furaldehyde (**2a**) were selected as typical starting points and calculations were carried out using the CNDOVSB method[7] throughout to assess the effect of increasing conjugation on the spectrum, dipole moment, and hyperpolarisability of the alkenyl derivatives (**1f**–**i** and **2b**–**e**) as in previous studies on donor–acceptor arenes and alkenes[10,12] where the calculated results have shown a close correlation with experimental data from electric field induced second harmonic generation in solution.

Molecular Structures.—The structures of all the molecules considered here were optimised fully using the AM1 method[16] of the MOPAC program.[17] Initial calculations were also carried on 4-methoxybenzaldehyde (**1e**) using the 3-21G basis set[18] of the GAMESS program.[19] The numbering convention adopted for the heavy atoms is shown in Fig. 1.

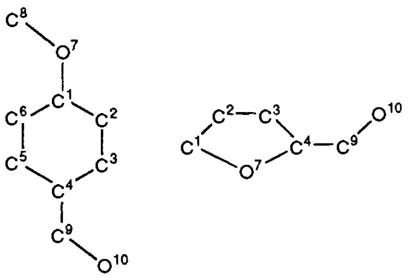


Fig. 1 Numbering convention adopted for the *trans*-conformers of 4-methoxybenzaldehyde (**1e**) and 2-furaldehyde (**2a**)

Discussion

Structures and Conformations.—There are two possible conformations for 4-methoxybenzaldehyde (**1e**): (1) where the methyl group and carbonyl oxygen atom lie either on the same side of the benzene ring (*cis*); or (2) on opposite sides (*trans*). A similar situation arises for 2-furaldehyde (**2a**) where the carbonyl group either points down towards the heterocyclic oxygen (*cis*) or upwards in the opposite direction (*trans*). Full optimisation of both conformers for each molecule using the AM1 method strongly suggests that there is little energy difference between them with the furan (**2a**) showing the largest value of around 0.9 kcal mol^{-1} in favour of the *trans*-conformer (Table 2).* The geometries so obtained for each conformer are essentially identical in terms of bond lengths and angles, and the data obtained for the furan (**2a**) is fully consistent with that found in the Cambridge Structural Database[20] for other simple furans.

In the absence of crystallographic data on the benzaldehyde (**1e**) itself, the structure of the molecule was calculated also at the more accurate *ab initio* 3-21G level to provide an independent check on the accuracy of the semi-empirical method. The results from the *ab initio* calculation suggest that the AM1 method overestimates the key C-1–O-7 and C-9–O-10 bond lengths with values of 1.378 and 1.234 Å for the latter, and 1.363 and 1.212 Å for the former (Table 2). However, a comparison between the calculated and experimental dipole moment indicate that the 3-21G method over-estimates its value by a substantial margin with a value of 5.08 D suggesting that the structure may not be particularly accurate. In contrast, the AM1 results at 2.78 (*cis*-conformer) and 4.14 (*trans*-conformer) are closer to the experimental value of 3.26 D and suggest that in solution, the benzaldehyde (**1e**) may be a mixture of the *cis* and *trans* conformers. This is supported by the experimental data for 2-furaldehyde (**2a**)[14] where the solution value of 3.58 D is exactly the average of the experimental *cis* and *trans* isomer values of 3.92 and 3.23 D respectively. Overall, the results obtained with the AM1 method appear to give a reasonable account of the geometries of both aldehydes (**1e**) and (**2a**) and

---

* 1 cal = 4.18 J.

Table 2 Geometries and dipole moments calculated for the *cis*- and *trans*-conformers of 2-furaldehyde (**2a**) and 4-methoxybenzaldehyde (**1e**) using the AM1 and 3-21G methods

	2a		**1e**		
Geometric variable[a]	*cis*	*trans*	*cis*	*trans*	3-21G[b]
C-1–C-2	1.385	1.383	1.401	1.409	1.395
C-2–C-3	1.441	1.443	1.393	1.387	1.371
C-3–C-4	1.388	1.386	1.399	1.404	1.393
C-4–C-5			1.404	1.399	1.379
C-5–C-6			1.387	1.392	1.383
C-6–C-1			1.410	1.402	1.384
C-1–O-7	1.387	1.387	1.378	1.378	1.363
O-7–C-8			1.424	1.424	1.439
C-4–C-9	1.455	1.455	1.468	1.468	1.467
C-9–O-10	1.230	1.232	1.234	1.234	1.212
C-1–C-2–C-3	106.5	106.4	119.2	119.2	119.9
C-2–C-3–C-4	106.8	107.0	120.7	120.7	120.3
C-3–C-4–C-5			119.6	119.6	119.5
C-4–C-5–C-6			120.6	120.7	120.7
C-5–C-6–C-1			119.2	119.2	119.6
C-6–C-1–C-2			120.8	120.8	120.0
C-1–O-7–C-8			116.4	116.4	120.9
C-2–C-1–O-7	110.5	110.7	124.5	114.8	116.3
C-3–C-4–C-9	132.1	134.4	120.6	120.5	119.9
C-4–C-9–O-10	124.6	122.6	123.8	123.8	124.6
ΔH_f[c]	−25.05	−25.96	−47.59	−47.46	
μ_{calc}[d]	3.42	2.88	2.78	4.14	5.08
μ_{exp}[d,e]	3.92	3.23	3.26	3.26	3.26

[a] Bond lengths in angstroms, angles in degrees. [b] Full optimisation for the *trans*-isomer. [c] In kcal mol^{-1}. [d] In debyes. [e] From ref. 14.

Table 3 Calculated transition energies, dipole moments, and hyperpolarisabilities of the arylpolyenals **1** and **2**[a]

Structure	n	μ	λ	f	$\Delta\mu$	β_0	$\beta_{1.17}$
1e	0	4.14	268	0.72	4.76	4.28	6.29
f	1	4.88	321	1.16	6.38	11.32	21.44
g	2	5.24	366	1.60	6.90	21.65	55.93
h	3	5.46	404	2.05	7.23	38.66	136.21
i	4	5.61	437	2.46	7.48	57.80	296.12
2a	0	2.88	274	0.56	3.74	2.21	3.52
b	1	3.42	337	0.96	5.54	9.69	20.46
c	2	3.67	383	1.38	6.59	21.76	64.38
d	3	3.81	420	1.82	7.24	39.10	161.69
e	4	3.91	451	2.25	7.71	60.07	374.63

[a] μ is the AM1 dipole moment in debye; λ is the transition energy (in nm), f is the oscillator strength, $\Delta\mu$ is the difference between ground and excited state dipole moment (in D); β_0 and $\beta_{1.17}$ are the vector components of the molecular hyperpolarisabilities at zero field and 1.17 eV respectively (expressed in units of 10^{-30} cm^5 esu^{-1}), all calculated at the CNDOVSB level.[7]

the method was then adopted for the alkenyl derivatives (**1f**–**i** and **2b**–**e**).

The insertion of a single alkene unit between the respective aromatic ring and the aldehyde group multiplies the conformational possibilities. For example, the furan (**2b**) is able to adopt at least four stable conformations where the alkene group either adopts a *cis* or *trans* conformation with the adjacent double bond of the furan ring, with the terminal carbonyl oxygen atom either *cis* or *trans* to the heterocyclic oxygen. AM1 calculations suggest that the *cis–trans* conformation is the most stable with a calculated heat of formation of -12.8 kcal mol^{-1} compared with values of -12.6, -12.6 and -12.3 kcal mol^{-1} for the *cis–cis*, *trans–trans* and *trans–cis* isomers, respectively. Because one important SHG application of the molecules involves electric field poling to induce non-centrosymmetric orientation, the conformations with the largest dipole moments are more likely to be favoured. For this reason, the *cis–trans* conformation was selected for subsequent calculation of the hyperpolarisability, and the structures of the remaining furylalkenals (**2c**–**e**) were calculated with the additional double bonds placed *trans* to the first double bond. For the same reason, the structures of the 4-methoxyphenylalkenyls (**1f**–**i**) were calculated also as the *trans*-conformers.

Calculated Spectroscopic Properties.—The insertion of an alkenyl group between the aromatic ring and the aldehyde acceptor in 4-methoxybenzaldehyde (**1e**) to give 4-methoxycinnamaldehyde (**1f**) results in a substantial bathochromic shift in the predicted absorption band to 321 nm in line with the experimental value[21] of 322 nm (Table 3). There is also a large increase in the oscillator strength reflecting the increased conjugation, and the ground state dipole moment also rises from 4.14 to 4.88 D respectively. The insertion of further alkenyl groups results in a further bathochromic shift in the absorption bands, and an increase in both the oscillator strengths and ground state dipole moments though the effect appears to saturate with increasing chain length. A similar pattern emerges in the change from 2-furaldehyde (**2a**) to 2-furylacrolein (**2b**) where the absorption band moves from 274 to 337 nm, and the dipole moment increases from 2.88 to 3.42 D.

The calculated absorption maxima which increase with increasing chain length, however, are over-estimated relative to the experimental data[22] (Table 1). This is especially true with the extended members of both series and a similar effect has noted in spectroscopic calculations on the corresponding *N*,*N*-dimethylaminopolyenals[15] where the empirical structures used for calculation especially at extended chain length were thought to contribute to the error. However, in this case, the structures have all been calculated in a self-consistent manner and this error should not arise. The explanation for this over-estimation, therefore, particularly for the furylalkenals (**2**), is not entirely clear, but the greater solubility of the *cis*-conformers of *N*,*N*-dimethylaminopolyenals over the *trans*-forms at longer chain length suggests that the experimental absorption data obtained in solution may relate to the former rather than the latter which have been calculated here.[21]

Calculated Hyperpolarisabilities.—The calculated hyperpolarisabilities of both the 4-methoxyphenylalkenals (**1e**–i) and furylalkenals (**2a**–**e**) rise sharply with the insertion of a single alkenyl group to give values (in units of 10^{-30} cm^5 esu^{-1}) for the phenylpolyenal (**1f**) of 11.3 (at zero field) and 21.4 (at an applied field of 1.17 eV) which are comparable to those calculated for strong donor–acceptor systems such as *N*,*N*-dimethyl-4-nitroaniline (**1b**) which has values[15] of 12.3 and 24.6 at the same field strengths (Table 3). Similar values are calculated for 2-furylacrolein (**2b**). Further alkenyl groups positioned between the aldehyde and aryl rings result in much larger hyperpolarisabilities but the molecules are no longer transparent at the critical SHG wavelengths. The best compromise between transparency and hyperpolarisability appears to be the use of one or two alkenyl group as in the 4-methoxyphenylalkenals (**1f** and **g**) and the furylalkenals (**2b** and **c**). The calculated hyperpolarisabilities and absorption spectra of these extended molecules appear to be fully comparable with other strong donor–acceptor systems though they suffer from the disadvantage of their conformational flexibility and reduced stability particularly with regard to their use in polymeric systems.

Conclusions

The calculated hyperpolarisabilities of the 4-methoxyphenylalkenals (**1f**–i) and the furylalkenals (**2a**–**e**) increase with increasing conjugation pathlength between the aromatic ring and the terminal aldehyde group. The initial members of the series in both cases are transparent, possess relatively large hyperpolarisabilities, and have potential application as materials for second harmonic generation.

References

1 *Nonlinear Optical Effects in Molecules and Polymers*, eds. P. N. Prasad and D. J. Williams, Wiley, New York, 1991.
2 *Nonlinear Optics of Organics and Semiconductors*, ed. K. Kobayashi, Springer-Verlag, Tokyo, 1989.
3 *Nonlinear Optical Properties of Organic Molecules and Crystals*, eds. D. S. Chemla and J. Zyss, Academic Press, New York, 1987.
4 *Nonlinear Optical and Electroactive Polymers*, eds. P. N. Prasad and D. R. Ulrich, Plenum Press, New York, 1988.
5 J. A. Morrell and A. C. Albrecht, *Chem. Phys. Lett.*, 1979, **64**, 46.
6 S. J. Lalama and A. F. Garito, *Phys. Rev. A*, 1979, **20**, 1179.
7 V. J. Docherty, D. Pugh and J. O. Morley, *J. Chem. Soc., Faraday Trans. 2*, 1985, **81**, 1179.
8 C. W. Dirk, R. J. Tweig and G. Wagniere, *J. Am. Chem. Soc.*, 1986, **108**, 5387.
9 DeQuan Li, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, 1988, **110**, 170.
10 J. O. Morley and D. Pugh, *J. Chem. Soc., Faraday Trans. 2*, 1991, **87**, 3021.
11 J. Ward, *Rev. Mod. Phys.*, 1965, **37**, 1.
12 J. O. Morley, V. J. Docherty and D. Pugh, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1357.
13 J. P. Phillips, L. D. Freedman and J. C. Craig, *Organic Electronic Spectral Data*, Interscience, New York, 1963, vol. I–X.
14 A. L. McClellan, *Tables of Experimental Dipole Moments*, W. H. Freeman, San Francisco, 1963, vol. I; Rahara Enterprises, San Francisco, 1974, vol. II.
15 J. O. Morley, V. J. Docherty and D. Pugh, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1351.
16 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1986, **107**, 3902.
17 QCPE Program 455 Version 6.0, Department of Chemistry, Indiana University, Bloomington, IN 47405, USA.
18 See *e.g.*, W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986.
19 M. F. Guest and P. Sherwood, GAMESS, an *ab initio* program, Daresbury Laboratory, Warrington, UK.
20 Cambridge Structural Database, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 2EW, UK.
21 D. Marshall and M. C. Whiting, *J. Chem. Soc.*, 1956, 4082.
22 E. R. Blout and M. Fields, *J. Am. Chem. Soc.*, 1948, **70**, 189.
23 J. O. Morley, *J. Chem. Soc., Faraday Trans.*, in press.

Paper 4/00693C
Received 4th *February* 1994
Accepted 15th *March* 1994