# Effects of conformation, substituents and solvent on molecular hyperpolarizabilities of push–pull diaryl-alkenes and -dienes: a computational study

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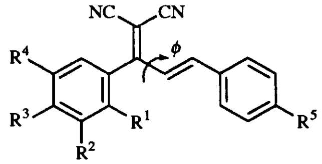
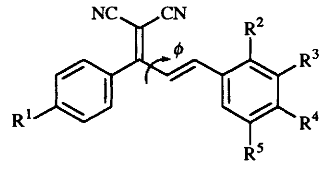
The effects of substituents [donor strength ($NMe_2$ *vs.* MeO), number as well as positional isomerism], conformation (*E*/*Z* isomerism with respect to formal single bonds) and solvent on molecular first-order hyperpolarizabilities, $\beta$, of a series of differently substituted push–pull dicyanomethylenediaryl-alkenes (**1–21**) and -dienes (**23–25**) is discussed with the aid of semiempirical molecular orbital calculations (AM1 for structures, INDO/S for spectroscopic properties and hyperpolarizabilities). Without exception *E*-isomers are calculated to be slightly more stable and to have higher hyperpolarizabilities. The effect on both excitation energies and $\beta$ of a fairly polar solvent (acetone) is found to be rather pronounced. Methoxy substitution of the arylalkenyl moiety leads to higher hyperpolarizabilities than the isomeric substitution of the aryl group (**1–8** *vs.* **9–21**). Extension of the chromophore by a second arylalkenyl group (**10** *vs.* **22**; **20** *vs.* **23**) or introduction of an additional donor (**22** *vs.* **24**; **23** *vs.* **25**) decreases $\beta$.

## Introduction

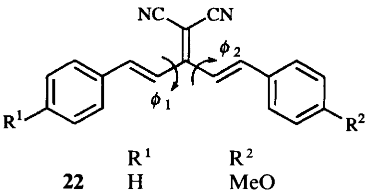
Donor–acceptor substituted conjugated organic compounds offer great promise as materials for non-linear optic devices.[1] The required high first-order molecular hyperpolarizabilities [$\beta(-2\omega,\omega,\omega)$ for second-order processes] can be obtained by increasing the length of the conjugated chain (*e.g.*, in push–pull polyenes and carotenoids an exponential dependence of $\beta$ on the number of double bonds has been established).[2] However, for second harmonic generation (SHG), where the emission from a semiconductor laser is converted from the infrared to the blue region, practically useful materials must be transparent at the SHG wavelength to avoid losses by self-absorption. This requirement puts some restrictions on the extension of the conjugated system to achieve higher non-linearities. Alternatively, changing the donor or acceptor strength, *e.g.* replacing aryl by heteroaryl groups[3] or a carbonyl by cyanovinyls,[4] might be used to enhance the hyperpolarizabilities. In contrast to enlarging the conjugated system the effects of such modifications are less clearcut. Specifically, a 'saturation' effect has been predicted theoretically and recently confirmed by experiment.[5] In other words, for a given chromophore, there exists an optimal donor–acceptor combination.[6] Increasing either the strength of the donor and/or the acceptor does not necessarily lead to a corresponding increase in molecular hyperpolarizabilities.[7] To address the question as to whether this optimal donor–acceptor combination already has been found as well as a general guide in the design of organic molecules with high non-linear optical properties, computational methods have become increasingly important.[8–12] Here we present a theoretical study of a promising class of compounds **1–25**. These molecules have been chosen for the following reasons: (*i*) recently, it has been shown that vanillin and polyenovanillin derivatives might represent an interesting new class of hyperpolarizable compounds;[12] (*ii*) methoxy groups are weaker donors than the more commonly used *N*,*N*-dimethylamino group and, thus, should provide a sufficient hypsochromic shift to avoid self-absorption of the SHG frequency;[12] (*iii*) molecules of this type are also useful as speciality dyes;[13] and (*iv*) to be practically useful, simple synthetic methods should be readily available.[13] Based on the results of the computations the effect of substituents (number and positional isomerism, donor strength), conformation [each one of compounds **1–21** can exist as the *E* ('s-trans') or *Z* ('s-cis') isomer with respect to torsion around the formal single bond



| | R1 | R2 | R3 | R4 | R5 |
|---|---|---|---|---|---|
| **1** | H | MeO | MeO | MeO | H |
| **2** | MeO | H | H | MeO | H |
| **3** | H | MeO | MeO | H | H |
| **4** | H | H | $NMe_2$ | H | H |
| **5** | H | MeO | MeO | MeO | MeO |
| **6** | MeO | H | H | MeO | MeO |
| **7** | H | MeO | MeO | H | MeO |
| **8** | H | H | $NMe_2$ | H | MeO |



| | R1 | R2 | R3 | R4 | R5 |
|---|---|---|---|---|---|
| **9** | MeO | MeO | H | H | H |
| **10** | H | H | H | MeO | H |
| **11** | MeO | H | MeO | MeO | H |
| **12** | MeO | MeO | H | H | MeO |
| **13** | H | MeO | H | H | MeO |
| **14** | H | MeO | H | H | H |
| **15** | MeO | H | MeO | MeO | MeO |
| **16** | MeO | H | H | MeO | H |
| **17** | MeO | H | H | H | H |
| **18** | H | H | MeO | MeO | H |
| **19** | H | H | MeO | MeO | MeO |
| **20** | H | H | H | $NMe_2$ | H |
| **21** | MeO | H | H | $NMe_2$ | H |



| | R1 | R2 |
|---|---|---|
| **22** | H | MeO |
| **23** | H | $NMe_2$ |
| **24** | MeO | MeO |
| **25** | $NMe_2$ | $NMe_2$ |

**Table 1** Calculated heats of formation, $\Delta_f H$ (kcal mol$^{-1}$), dipole moments, $\mu$ (debye), excitation energies, $\nu$ (cm$^{-1}$) and oscillator strengths, $f$

| | AM1 | | ZINDO | | | ZINDO-SCRF$^a$ | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $\Delta_f H$ | $\mu$ | $\mu$ | $\nu$ | $f$ | $\mu$ | $\nu$ | $f$ |
| (*E*)-**1** | 35.8 | 4.37 | 6.37 | 28 816 | 0.64 | 8.89 | 27 765 | 0.54 |
| (*E*)-**2** | 71.5 | 6.51 | 8.87 | 30 505 | 1.21 | 12.47 | 28 996 | 1.09 |
| (*E*)-**3** | 70.8 | 3.89 | 5.87 | 27 517 | 0.44 | 8.52 | 26 088 | 0.39 |
| (*E*)-**4** | 152.3 | 6.79 | 8.90 | 28 449 | 0.64 | 13.56 | 26 862 | 0.53 |
| (*E*)-**5** | −2.6 | 3.73 | 5.59 | 27 866 | 1.04 | 8.60 | 26 349 | 1.07 |
| (*E*)-**6** | 33.2 | 5.57 | 8.15 | 28 510 | 1.24 | 11.74 | 25 986 | 0.11 |
| (*E*)-**7** | 32.4 | 3.33 | 5.57 | 27 374 | 0.77 | 8.41 | 26 055 | 1.03 |
| (*E*)-**8** | 113.9 | 6.09 | 8.54 | 27 857 | 0.97 | 13.26 | 25 203 | 1.03 |
| (*E*)-**9** | 69.4 | 5.27 | 7.52 | 28 080 | 0.74 | 11.25 | 26 282 | 0.72 |
| (*E*)-**10** | 105.6 | 7.00 | 9.70 | 28 064 | 1.15 | 16.27 | 23 858 | 1.06 |
| (*E*)-**11** | 32.7 | 4.97 | 7.55 | 27 728 | 0.98 | 11.66 | 24 699 | 0.90 |
| (*E*)-**12** | 32.8 | 5.75 | 8.38 | 27 228 | 0.54 | 12.39 | 24 234 | 0.42 |
| (*E*)-**13** | 71.1 | 6.40 | 9.16 | 27 010 | 0.55 | 14.42 | 22 642 | 0.38 |
| (*E*)-**14** | 107.8 | 5.80 | 8.08 | 28 208 | 0.81 | 12.96 | 25 154 | 0.71 |
| (*E*)-**15** | −2.5 | 3.58 | 5.84 | 28 291 | 0.84 | 8.33 | 26 836 | 0.88 |
| (*E*)-**16** | 67.2 | 4.82 | 7.24 | 27 960 | 1.03 | 11.38 | 25 468 | 1.07 |
| (*E*)-**17** | 105.6 | 5.34 | 7.49 | 28 594 | 0.65 | 11.36 | 27 366 | 0.59 |
| (*E*)-**18** | 71.2 | 6.71 | 9.53 | 27 357 | 1.06 | 14.75 | 23 504 | 0.90 |
| (*E*)-**19** | 36.1 | 6.78 | 9.77 | 28 574 | 1.02 | 14.25 | 25 337 | 0.87 |
| (*E*)-**20** | 151.8 | 7.65 | 9.53 | 27 294 | 1.20 | 17.48 | 21 931 | 1.11 |
| (*E*)-**21** | 113.8 | 6.06 | 7.84 | 27 707 | 1.06 | 12.15 | 24 756 | 1.06 |
| (*E,E*)-**22** | 117.6 | 5.64 | 7.83 | 27 356 | 1.02 | 12.96 | 24 318 | 0.85 |
| (*E,E*)-**23** | 164.4 | 7.48 | 9.76 | 27 460 | 1.04 | 16.43 | 23 544 | 0.85 |
| (*E,E*)-**24** | 79.3 | 4.83 | 7.10 | 27 317 | 1.04 | 11.37 | 26 028 | 0.94 |
| (*E,E*)-**25** | 172.6 | 6.94 | 8.37 | 27 040 | 1.10 | 13.14 | 25 254 | 0.95 |

$^a$ Acetone as solvent.

(indicated by the dihedral angle $\varphi$) four rotamers are possible for **22** and **23** and three for **24** and **25**] and solvation (the importance of including solvent effects in the calculation of hyperpolarizabilities has recently been pointed out)[14] will be discussed.

## Results and discussion

### Molecular structures and conformations

The structures of all the molecules were calculated by the AM1 method.[15] This method has been chosen because of its computational efficiency as well as to provide sufficient accuracy in problems of this kind.[12,16] The results of these calculations (heats of formation $\Delta_f H$ (kcal mol$^{-1}$; 1 cal = 4.18 J) and dipole moments (debye) are collected in Table 1 (according to the suggestion of one referee only the most stable conformation is included). Energy differences between *E* and *Z* rotamers are rather small with the *E* isomer being slightly more stable. An equilibrium of both conformations with the *E* form slightly dominating thus appears reasonable. For almost all compounds a higher dipole moment for this latter structure is obtained which, in solution, should lead to an additional stabilization of the *E*-rotamer. Dipole moments calculated by INDO/S[17] are generally somewhat larger, the overall trend corresponds to the AM1 values (see Table 1). In the case of **21**–**25** the *E,E* and *Z,Z* conformers are calculated to be, respectively, the most and least stable ones.

### Excitation energies

UV–VIS spectroscopic properties (wavenumbers, $\nu$, and oscillator strengths, $f$) were obtained by INDO/S[17] both for isolated molecules as well as in solution. Solvent effects were treated by the self-consistent-reaction-field method (SCRF);[18] acetone was used as a dipolar aprotic solvent (hydrogen bonding effects are of course beyond the scope of the SCRF method). The results (first electronic transition with $f > 0.1$) are also given in Table 1. For the isolated molecules the calculations predict absorptions at quite short wavelengths. Inclusion of the solvent effect has a rather profound bathochromic effect. More importantly, the response of the various compounds to solvation differs markedly. Any comparison of isolated molecule calculations with experimental UV–VIS spectra in polar solutions, therefore, must fail. With respect to *E*/*Z*-isomerism, the *s-trans* (*E*) rotamers (**2** being the only exception) are calculated to absorb at longer wavelengths ($\approx$ 1000 cm$^{-1}$). For **22**–**25** the *Z,Z* conformers should absorb at the shortest wavelength. Interestingly, introduction of a second donor in **22** and **23** to give **24** and **25**, respectively, should lead to a hypsochromic shift (see Table 1). The excitation energies of compounds (*E*)-**10**, **13**, **18**, **20** and **23** are calculated to be—at least in polar media—already in the region where self-absorption of the SHG frequency could occur.

### Hyperpolarizabilities

Frequency dependent first-order hyperpolarizabilities [at excitation energies of 0.0 ($\beta_0$) and 1.17 eV ($\beta_{1.17}$)] were obtained by means of the INDO/S[17] sum-over-states (SOS)[8,9] method. Static hyperpolarizabilities were also computed by the Tamm–Dancoff[19] (single excitation CI, $\beta_{\mathrm{TDA}}$) and random phase ($\beta_{\mathrm{RPA}}$)[20] approximations. The results {$\beta_\mu$, *i.e.* projection of $\beta$ onto the molecular dipole moment [eqns. (1), (2)]} are collected in Table 2 (according to a suggestion of one referee, only the conformation with the higher $\beta$-values are included). From the data presented in Table 2 one can draw the following

$$\beta_\mu = \sum_i \beta_i \mu_i / \|\mu\| \qquad (1)$$

$$\beta_i = \tfrac{1}{3}\sum_j (\beta_{ijj} + \beta_{jij} + \beta_{jji});\ i,j = x,y,z \qquad (2)$$

conclusions. (*i*) With respect to the conformation, *E*-isomers generally are not only more stable but also have higher values

**Table 2** Calculated hyperpolarizabilities, $\beta$ ($10^{-30}$ cm$^5$ esu$^{-1}$)

| | ZINDO | | | | ZINDO-SCRF[a] | | | |
|---|---|---|---|---|---|---|---|---|
| Compound | $\beta_{TDA}$ | $\beta_{RPA}$ | $\beta_0$ | $\beta_{1.17}$ | $\beta_{TDA}$ | $\beta_{RPA}$ | $\beta_0$ | $\beta_{1.17}$ |
| (*E*)-**1** | 4.7 | 5.5 | 4.7 | 10.7 | 8.9 | 9.5 | 8.8 | 21.4 |
| (*E*)-**2** | 1.6 | 2.8 | 1.6 | 4.6 | 6.5 | 7.6 | 6.6 | 16.9 |
| (*E*)-**3** | 6.0 | 6.7 | 6.0 | 14.6 | 11.1 | 11.5 | 11.1 | 28.3 |
| (*E*)-**4** | 5.9 | 6.7 | 5.7 | 13.4 | 15.0 | 15.2 | 14.9 | 38.7 |
| (*E*)-**5** | 11.8 | 12.4 | 11.8 | 29.6 | 21.6 | 21.4 | 21.5 | 61.8 |
| (*E*)-**6** | 8.0 | 9.1 | 8.0 | 21.0 | 19.7 | 20.0 | 19.7 | 60.7 |
| (*E*)-**7** | 12.9 | 13.4 | 12.8 | 32.4 | 24.4 | 24.0 | 24.3 | 72.2 |
| (*E*)-**8** | 12.0 | 12.6 | 12.0 | 29.7 | 30.5 | 29.5 | 30.3 | 101.8 |
| (*E*)-**9** | 5.0 | 6.4 | 4.9 | 13.6 | 13.6 | 14.2 | 13.6 | 40.1 |
| (*E*)-**10** | 10.4 | 11.1 | 10.3 | 26.7 | 41.4 | 38.8 | 41.4 | 186.0 |
| (*E*)-**11** | 13.7 | 13.7 | 13.6 | 33.2 | 33.3 | 31.4 | 33.2 | 115.0 |
| (*E*)-**12** | 6.6 | 7.4 | 6.4 | 17.2 | 17.8 | 17.7 | 17.8 | 61.5 |
| (*E*)-**13** | 6.9 | 7.8 | 6.7 | 19.0 | 26.7 | 25.4 | 26.6 | 134.2 |
| (*E*)-**14** | 4.8 | 6.1 | 4.8 | 13.9 | 19.6 | 19.5 | 19.7 | 68.5 |
| (*E*)-**15** | 10.5 | 10.4 | 10.4 | 24.8 | 18.2 | 17.4 | 18.2 | 49.3 |
| (*E*)-**16** | 11.6 | 12.3 | 11.5 | 28.7 | 28.3 | 27.6 | 28.2 | 90.8 |
| (*E*)-**17** | 4.9 | 5.9 | 4.9 | 11.4 | 11.9 | 12.4 | 12.0 | 30.0 |
| (*E*)-**18** | 11.2 | 11.4 | 11.0 | 29.4 | 33.4 | 31.4 | 33.2 | 143.1 |
| (*E*)-**19** | 8.1 | 8.3 | 8.2 | 20.7 | 22.3 | 21.1 | 22.5 | 74.9 |
| (*E*)-**20** | 16.0 | 16.2 | 15.8 | 43.0 | 80.4 | 70.4 | 80.2 | 697.4 |
| (*E*)-**21** | 12.8 | 13.2 | 12.7 | 32.4 | 33.5 | 32.2 | 33.7 | 119.0 |
| (*Z*,*E*)-**22** | 12.2 | 12.6 | 12.1 | 30.3 | 33.8 | 32.1 | 33.7 | 122.2 |
| (*Z*,*E*)-**23** | 13.2 | 13.4 | 13.2 | 34.3 | 45.5 | 42.4 | 45.5 | 208.9 |
| (*E*,*Z*)-**24** | 13.8 | 14.1 | 13.9 | 34.7 | 29.9 | 28.9 | 30.0 | 97.8 |
| (*E*,*E*)-**25** | 17.3 | 17.6 | 17.1 | 44.9 | 33.8 | 33.1 | 33.9 | 110.2 |

[a] Acetone as solvent.

of the first-order hyperpolarizability (this observation holds without exception when solvation is taken into account). Synthesis of compounds with fixed *E*-conformation, therefore, should be preferred. (*ii*) A polar solvent (here illustrated by acetone) leads to a significant enhancement of $\beta$ {normally, by a factor of two, in some cases [*e.g.* (*E*)-**20**] much larger effects are found}. (*E*)-Isomers seem to be more prone to solvent effects thus stressing the importance of conformationally rigid structures. (*iii*) Comparing analogously substituted compounds of the series **1**–**8** with those of **9**–**21** one can clearly see that substitution of the aromatic ring in the arylalkenyl group is to be preferred when high $\beta$ values are desired (see **1** *vs.* **19**, **2** *vs.* **13**, **3** *vs.* **18**, **4** *vs.* **20**, **7** *vs.* **11** and **8** *vs.* **21**; for the pair **5**–**15**, compound **5** has a higher calculated $\beta$ value). (*iv*) Within the series **1**–**8** those ones with $R^5$ = MeO have higher $\beta$-values than those with $R^5$ = H (**1** *vs.* **5**, **2** *vs.* **6**, **3** *vs.* **7**, **4** *vs.* **8**). In complete contrast, for **9**–**21**, the analogous structural modification with $R^1$ = H is to be preferred over $R^1$ = MeO (**9** *vs.* **14**, **11** *vs.* **18**, **12** *vs.* **13**, **15** *vs.* **19**, **16** *vs.* **10**, **21** *vs.* **20**). (*v*) As one might expect, a *para*-methoxy group ($R^4$ = MeO) seems to be an essential requirement for high $\beta$-values (see *e.g.*, **17** *vs.* **9** *vs.* **16**). If there is already a *para*-MeO present, additional donors either do not lead to a further increase at all (**10** *vs.* **18** *vs.* **19**; $R^1$ = H) or, for $R^1$ = MeO, lead to a maximum of $\beta$ for *meta*,*para*-disubstitution (**11** *vs.* **15** *vs.* **16**). Similarly, *ortho*,*meta*- is less effective than *meta*, *para*-disubstitution (**11** *vs.* **12**). (*vi*) As usual, a higher donor strength (**10** *vs.* **20**, **16** *vs.* **21**) greatly enhances the hyperpolarizabilities (compound **20**, however, is calculated to absorb in the region where self-absorption of the SHG frequency might occur). (*vii*) Extension of the chromophore by a second arylalkenyl rather than aryl group should lead to a decrease in the hyperpolarizability (**10** *vs.* **22**; **20** *vs.* **23**); similarly, introduction of a second donor in **22** and **23** to give the symmetrically substituted derivatives **24** and **25** decreases $\beta$.

In summary, the results discussed above should represent useful guidelines for the synthesis of appropriately substituted molecules with high second-order optical non-linearities.

## Calculational details

Molecular structures were obtained by AM1[15] as implemented in the SYBYL molecular modelling package[21] with complete geometry optimization (the calculations were done in cartesian coordinates; the accuracy obtained with SYBYL-MOPAC is comparable to using the eigenvector following routine in standard MOPAC). Excitation energies and hyperpolarizabilities were calculated by INDO/S as implemented in the ZINDO package.[22]

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