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Structural effects influencing *cis–trans* isomerisation in methoxy and cyano substituted stilbene derivatives†

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Three substituted stilbenes were synthesised, and their photochemical *E–Z* isomerisation behaviour in solution studied. A rationalisation of the composition of the equilibrium mixture through the *ab initio* calculated energy difference between the electronic ground states of the isomers proved to be not possible. In contrast, the calculated energy differences agree quite well with the *E–Z* compositions obtained from the thermodynamic equilibrium, reached by thermal isomerisation in solution with a trace of iodine present. Additionally, X-ray structural information on the compounds studied is presented, and theoretical NMR shifts, calculated at the Hartree–Fock and density functional levels, have been used to assign the experimental ^{13}C NMR spectra of the new compounds.

Introduction

In our continuing research into semiconductor applications of arylene vinylene oligomers,[1–6] and into the isomerisation of thienylene vinylene dimers,[7] we synthesised 1-cyano-1,2-bis-(2-methoxyphenyl)ethene **1**, abbreviated CBMPE, 1-cyano-2-(2-methoxyphenyl)-1-phenylethene **2**, abbreviated CPMPE, and 1,2-bis(2-methoxyphenyl)ethene **3**, abbreviated BMPE, the structures of which are shown in Fig. 1. In our previous work on substituted 1,2-di-2-thienylethenes,[7] it was concluded that the photochemical *E–Z* isomerisation equilibrium is determined by the cyano and methoxy substituents. The isomer composition of the thienylethenes follows the NEER (Non-Equilibration of Excited Rotamers) principle,[8,9] that is the *E–Z* equilibrium can be rationalised from energy differences between electronic ground states of the energetically lowest conformations of the *E*- and *Z*-isomers. In the thienyl derivatives these energy differences are mainly governed by steric effects. In this work we will show that the values of the photochemical isomerisation for cyano and methoxy substituted stilbenes, **1**–**3**, differ greatly from the calculated *ab initio* ground state energy differences. The values for the iodine-catalysed, thermal isomerisation, however, will be shown to agree with the *ab initio* ground state energy differences. This is of interest, because compounds isomerising according to eqn. (1) have, in principle, potential as molecular switch materials.[10]

$$\textit{trans}\text{-isomer} \underset{\Delta T}{\overset{h\nu}{\rightleftarrows}} \textit{cis}\text{-isomer} \qquad (1)$$

In the nomenclature of the compounds **1**–**3** we follow strictly the standard IUPAC recommendations[11] regarding the use of *Z*/*E*. Note, however, that the classical *trans* steric relation of the phenyl groups, which is the main point of interest here, occurs not only in (*E*)-BMPE **3**, but also in (*Z*)-CBMPE **1** and (*Z*)-CPMPE **2**.

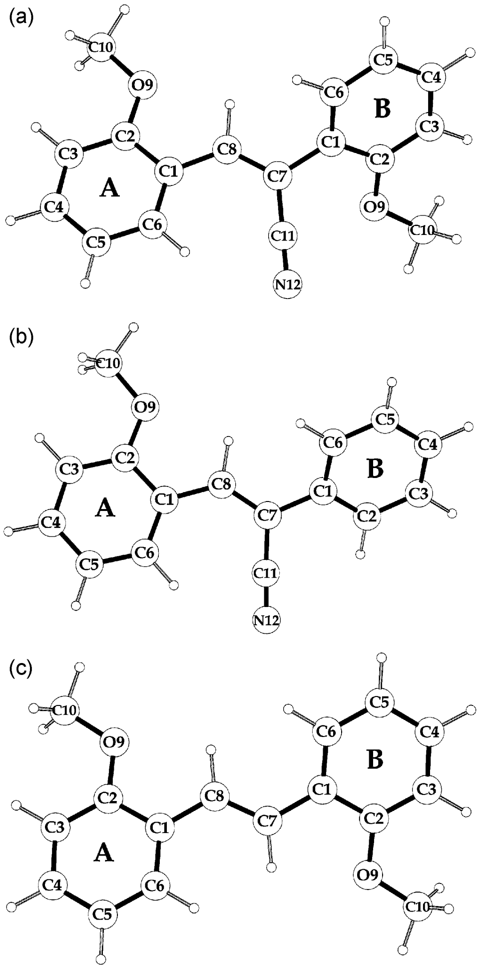

Fig. 1 Structural formula and atomic numbering of (*Z*)-CBMPE **1** (a), (*Z*)-CPMPE **2** (b) and (*E*)-BMPE **3** (c).

To maintain feedback between *ab initio* calculated geometries and energies, we performed single crystal X-ray determinations of **1** and **2**, revealing conformational and geometrical molecular details. Also, NMR chemical shifts were calculated at the Hartree–Fock and density functional (DFT) levels and used to obtain a complete assignment of the ^{13}C NMR spectra. Due to the asymmetry of the compounds and the resulting complexity

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† Electronic supplementary information (ESI) available: Cartesian coordinates for the calculated geometries of **1**–**3** and (*E*)- and (*Z*)-stilbene. See http://www.rsc.org/suppdata/p2/b2/b201623k/

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of the NMR spectra, 2D measurements would have been necessary for a complete assignment of these spectra. The approach we used circumvents the time-consuming recording of the hetero- and homonuclear 2D-resolved spectra and presents an equally rewarding alternative to a complete assignment based on experimental data alone. In addition to this, *ab initio* calculations can be of major importance in the determination of the configuration of trisubstituted ethenes.[12]

Experimental

Syntheses

All syntheses were carried out under a nitrogen atmosphere. Column chromatography was carried out on a silica column with 80 : 20 hexanes–ethyl acetate as the eluent, with the column wrapped in aluminium foil to minimise exposure to light during the separation. The fractions were kept cold and the solvent was evaporated as quickly as possible on a rotary evaporator. GC analyses were carried out on a Varian CP3380 with a CP-SIL-5 capillary column. GC–MS analyses were carried out on a CP-SIL-5 capillary GC column in an HP 5890-II GC, coupled to a Trio 2000 quadrupole mass spectrometer with Chemical Ionisation (CI), using methane as the ionising gas. NMR spectra were obtained in $CDCl_3$ with a Varian 400 MHz spectrometer. UV absorption and luminescence data were measured in methanol with Varian Cary 4 and Varian Cary Eclipse instruments. Melting points are uncorrected.

(*Z*)-CBMPE (1). Sodium (1.75 g, 0.05 mol) in ethanol (25 ml) was added dropwise to a stirred mixture of 2-methoxybenzaldehyde (6.8 g, 0.05 mol) and 2-methoxybenzyl cyanide (7.35 g, 0.05 mol), which was then refluxed for 2 h. Purification was achieved directly by column chromatography. Subsequent recrystallisation from a mixture of hexanes and ethyl acetate yielded the pure *Z*-isomer. The final yield was 2.8 g (21%); mp 104–106 °C; λ_{max}(abs) = 330 nm and λ_{max}(em) = 413 nm; δ_H (400 MHz, $CDCl_3$, TMS) 8.18 (1H, dd, $J = 7.8$, 1.38 Hz, H4B), 7.82 (1H, s, H8), 7.43 (1H, dd, $J = 7.62$, 1.67 Hz, H6B), 7.38 (1H, ddd, $J = 8.3$, 7.3, 1.5 Hz, H4A), 7.34 (1H, ddd, $J = 8.2$, 7.5, 1.7 Hz, H4B), 7.06 (1H, t, $J = 7.3$ Hz, H5A), 7.01 (1H, dt, $J = 7.5$, 1.1 Hz, H5B), 6.95 (1H, dd, $J = 8.3$, 0.8 Hz, H3B), 6.90 (1H, dd, $J = 8.3$, 0.7 Hz, H3A), 3.92 (3H, s, OCH_3–B), 3.85 (3H, s, OCH_3–A); δ_C see Table 3.

(*Z*)-CPMPE (2). Sodium (1.75 g, 0.05 mol) in ethanol (25 ml) was added dropwise to a stirred mixture of 2-methoxybenzaldehyde (6.8 g, 0.05 mol) and benzyl cyanide (5.8 g, 0.05 mol), which was then refluxed for 2 h. The reaction mixture was added to water (100 ml), which was extracted twice with CH_2Cl_2. After drying with $MgSO_4$, the solvents were evaporated on a rotary evaporator. The pure *Z*-isomer was obtained by column chromatography. The final yield was 4.8 g (40%); mp 45–47 °C; λ_{max}(abs) = 337 and λ_{max}(em) = 412 nm; δ_H (400 MHz, $CDCl_3$, TMS) 8.14 (1H, dd, $J = 7.8$, 1.5 Hz, H6A), 7.94 (1H, s, H8), 7.68 (2H, m, H2B–6B), 7.44–7.34 (4H, m, H4B/H3B–5B/H4A), 7.05 (1H, t, $J = 7.8$ Hz, H5A), 6.92 (1H, dd, $J = 8.40$, 0.9 Hz, H3A), 3.87 (3H, s, OCH_3); δ_C see Table 3.

(*E*)-BMPE (3). a) Sodium (0.2 g, 8.7 mmol), dissolved in a minimal amount of ethanol, was added dropwise to a stirred mixture of (2-methoxybenzyl)triphenylphosphonium chloride (3.3 g, 8.16 mmol) and 2-methoxybenzaldehyde (1.1 g, 8.16 mmol) in ethanol (50 ml) The reaction was left at room temperature overnight. 1.7 g of a white precipitate was filtered off (82%). GC showed this product to consist of a mixture of both isomers. b) Pure (*E*)-BMPE was synthesised by adding an excess of triethyl phosphite to 2-methoxybenzyl chloride (5 ml, 5.62 g, 0.0359 mol) and heating to 140 °C for 24 h. The excess triethyl phosphite was distilled off at reduced pressure and the resulting clear liquid (diethyl 2-methoxybenzylphosphonate) was used in the next step without further purification. 2-Methoxybenzaldehyde (5.38 g, 0.0396 mol) was added to the product of the previous step, as was a suspension of 60% NaH in mineral oils (1.7 g, 0.0425 mol). Dry THF (50 ml) was added to the mixture, resulting in an evolution of hydrogen gas. The reaction was kept at 60 °C for 20 h, the solvent was then distilled off under reduced pressure, and the product recrystallised from ethanol. The precipitate was filtered off and washed three times with ice-cold ethanol. Yield 5.8 g, pure according to GC. The overall yield is 67%; mp 136–137 °C (lit.,[13] 136–140 °C); λ_{max}(abs) = 329 and λ_{max}(em) = 388 nm. For NMR spectral data, see refs. 13 and 14.

X-Ray structure determination ‡

Crystals of (*Z*)-CBMPE **1** and (*Z*)-CPMPE **2**, suitable for X-ray diffraction, were obtained by slow evaporation of a saturated acetone solution. The crystal of (*Z*)-CPMPE **2** allowed us to establish the chemical structure unequivocally, but due to the very small crystal the data set contains only 70% of the expected reflections. Diffractograms were recorded on an Enraf-Nonius CAD4 diffractometer, using Mo-Kα radiation, and the structures solved using SHELXS97[15] and refined using SHELXL97.[16]

Crystal data for 1. $C_{17}H_{15}NO_2$, $M_w = 265.30$, orthorhombic, $a = 7.218(2)$, $b = 14.926(3)$, $c = 26.015(4)$ Å, $\alpha = \beta = \gamma = 90.00°$, $V = 2802.7(9)$ Å^3, $T = 294$ K, space group *Pbca* (no. 61), $Z = 8$, $D_c = 1.257$ g cm^{-3}, μ(Mo-Kα) = 0.083 mm^{-1}, 4073 unique reflections were measured and used in all calculations. Final R_1 (2760 $F_o > 4\sigma(F_o)$) was 0.0764 and wR (all F^2) was 0.1527.

Crystal data for 2. $C_{16}H_{13}NO$, $M_w = 235.27$, monoclinic, $a = 10.415(3)$, $b = 11.437(2)$, $c = 11.705(3)$ Å, $\alpha = \gamma = 90.00°$, $\beta = 113.86(2)$, $V = 1275.1(5)$ Å^3, $T = 294$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $D_c = 1.226$ g cm^{-3}, μ(Mo-Kα) = 0.077 mm^1, 2861 unique reflections were measured and used in all calculations. Final R_1 (1235 $F_o > 4\sigma(F_o)$) was 0.0611 and wR (all F^2) was 0.1862.

Isomerisation experiments

Isomerisation under thermodynamic conditions was performed in the dark by refluxing the compounds in *p*-xylene with a trace of iodine for four hours. A sample of the mixture was then analysed by GC, taking care that the solution was not exposed to light. Photochemical isomerisation took place in clear quartz cuvettes, in a darkened room, under a 6 W UV lamp (7 mW cm^{-2}) with a non-monochromatic emission band (maximum at 365 nm), in dry ethanol as solvent. Samples of the isomer mixture were taken at regular time intervals and analysed by GC, taking care that the solution was not exposed to light.

Geometry optimisations, energy and NMR calculations

Ab initio calculations at the Hartree–Fock level were perfomed using Pulay's gradient method[17] incorporated in the program BRABO for large molecules[18,19] with the 6-31G* basis set.[20–22] Geometries were calculated with complete relaxation until convergence was reached; for convergence criteria see reference 23. Starting from these geometries, further calculations were performed at the DFT/B3LYP/6-31G* level using GAUSSIAN 98.[24] At this level, Gibbs free energies were obtained from a standard frequency calculation, at $T = 293.15$ K and $p = 1$ atm. NMR shielding factors were calculated for all atoms using the GIAO method incorporated in GAUSSIAN 98 at the

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‡ CCDC reference numbers 179551–2. See http://rsc.org/suppdata/p2/b2/b201623k/ for crystallographic files in .cif or other electronic format.

HF/6-31+G* and B3LYP/6-31+G* levels, at the optimised B3LYP/6-31G* geometries. Calculated chemical shifts were obtained using the absolute shieldings of the carbon and the hydrogen atom of the reference compound, *i.e.* tetramethylsilane (TMS), which, based upon a B3LYP/6-31G* geometry, are tabulated as $\sigma_C = 200.1609$ ppm and $\sigma_H = 32.5272$ ppm at the HF/6-31+G* level[25] and were calculated as $\sigma_C = 190.9461$ ppm and $\sigma_H = 32.0980$ ppm at the B3LYP/6-31+G* level.

Results and discussion

Synthesis of the compounds

The new compound (*Z*)-CBMPE **1** is easily synthesised by a Knoevenagel condensation of 2-methoxybenzaldehyde with 2-methoxybenzyl cyanide, using sodium ethanolate as the base and a minimal amount of ethanol as the solvent. The reaction produces some by-products. After column chromatography and repeated crystallisations, the pure *Z*-isomer was obtained. A similar procedure, but without any solvent, yielded pure (*Z*)-CPMPE.[26–28] Its melting point (45–47 °C) is much lower than that of the product published by Jocelyn.[27] We believe that the latter product is the impure *E*-isomer. For BMPE[13,14] we used the standard procedure for a Wittig reaction: (2-methoxybenzyl)triphenylphosphonium chloride, prepared from commercially available 2-methoxybenzyl chloride, was reacted with 2-methoxybenzaldehyde to give a mixture of isomers in a yield of 82%. The analogous Wadsworth–Emmons reaction was also employed, which is reported to exclusively produce the *E*-product.[29] However, we obtained an impure compound, which gave pure (*E*)-BMPE **3** in a yield of 67% after recrystallisation from ethanol. Our NMR data are in agreement with the previously published values.[13,14] All recrystallised compounds were pure according to the gas chromatograms.

Ab initio calculations

The molecular framework and the atomic numbering of all three compounds are shown in Fig. 1; each hydrogen atom is assigned the same number as the carbon atom on which it is positioned. Coordinates and energies of the calculated structures can be found in the supplementary data. Calculations on the *Z*- and *E*-isomers of CBMPE **1** and of CPMPE **2** were performed without imposing planarity and structures with C_1 symmetry were indeed found. In the case of BMPE **3**, for both the *E*- and *Z*-isomers, C_2 symmetry was imposed during the refinement of the structure; subsequent frequency calculations indicated that the resulting structures were indeed energy minima. For (*Z*)-CBMPE **1**, the two conformers in which an attractive CH–*n*(O) interaction occurs between C(8)H and O(9A) are preferred.[7] Of these, the one in which the CN group is in the proximity of the OCH_3 on ring B [*r*C(11)–O(9B) = 2.794 Å (sum of Van der Waals radii[30] = 3.22 Å)], has the lowest energy (named [*ap*,*ap*] in Fig. 2, top). This may be the result of an attractive interaction between C(11) and O(9B), even though the torsion angle C(2B)–C(1B)–C(7–C(8) is 46°. The other conformer in which the ring B is rotated so that its OCH_3 group is located at the other side of the double bond—away from the CN group—is 3.93 kJ mol^{-1} higher in energy at the HF, and 1.21 kJ mol^{-1} at the DFT level (named [*ap*,*sp*] in Fig. 2, top). The calculated lowest energy conformer is also the one found in the solid. For the conformers of (*E*)-CBMPE **1**, similar arguments rationalise why the form named [*ap*,*ap*] in Fig. 2 (bottom) is 5.82 kJ mol^{-1} lower in energy at the HF and 2.22 kJ mol^{-1} at the DFT level than the form named [*ap*,*sp*] in Fig. 2 (bottom). Considering CPMPE **2** and BMPE **3** and using again the presence of one (in **2**) or two (in **3**) attractive CH–*n*(O) interactions leads to the lowest energy conformations of their *E* and *Z* configurations (see Figs. 3 and 4 respectively).

Table 1 contains the calculated energy differences between the lowest energy conformers of the *E*- and *Z*-configurations of each of the three compounds at the two levels of theory used: both the energy *E* at 0 K, and the Gibbs free energy *G* at 293.15 K, based on a classical calculation of the entropy term, are given. For each of these energy differences the resulting composition of the equilibrium mixture is calculated using the Boltzmann equation and the fraction of the *cis*-form of each of the three compounds is given in the table. It is clear that inclusion of the entropy term in the calculation of the energy differences, to obtain the relative free energies, has little effect on the position of the equilibrium.

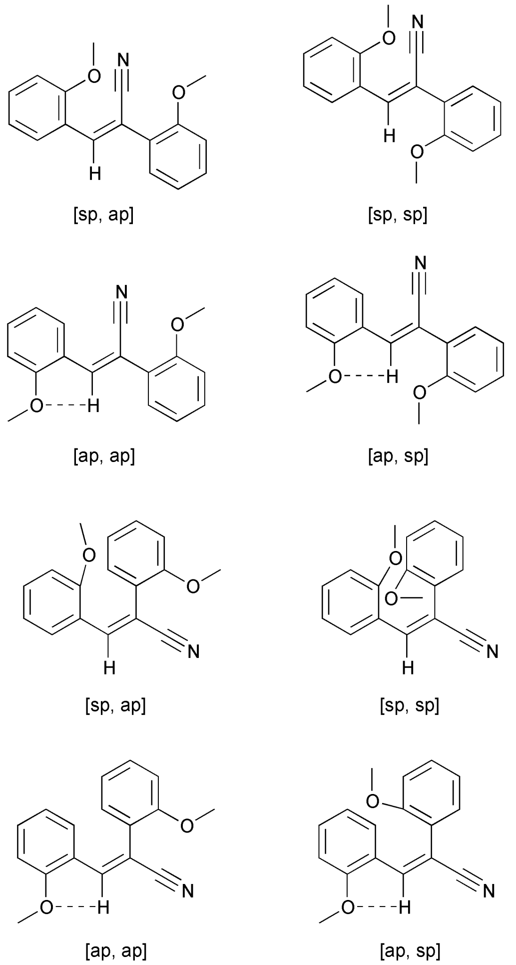

Fig. 2 Possible conformations for the *E*-(top) and *Z*-configurations (bottom) of CBMPE **1**. Planar forms are drawn for simplicity.

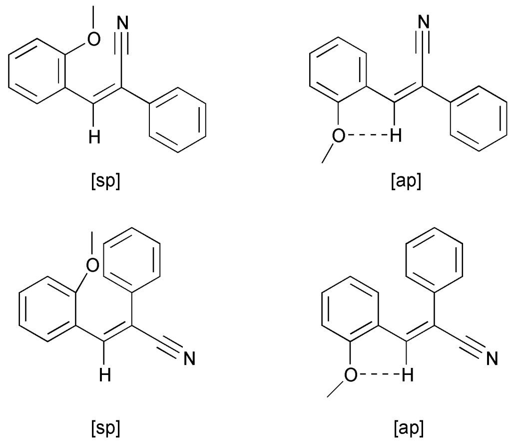

Fig. 3 Possible conformations for the *E*-(top) and *Z*-configurations (bottom) of CPMPE **2**. Planar forms are drawn for simplicity.

Selected calculated geometrical data on the three compounds have been compiled in Table 2 and will be discussed further in connection with the results from the X-ray crystal structure determination. Since it was used as a reference compound, data on stilbene are also included in the table. HF and DFT calculations on stilbene were performed, also imposing C_2 symmetry on both the *E* and the *Z* form. Again, the frequency calculations confirmed that the resulting structures were in fact energy minima.

Assignment of the NMR spectra

The values for ^{1}H NMR can be found in the Experimental section. Realising that the signal of H(6A) is shifted significantly downfield due to the close proximity of the nitrile group in (*Z*)-CPMPE **2**, the assignments of the ^{1}H NMR spectra of **1** and **2** are straightforward, based on increment calculations, comparison of coupling constants, integrations, and the published values for (*E*)-BMPE **3**. These assignments are completely reproduced by calculations of the chemical shifts at the HF level, which can be found in the Supplementary Information. Based on this agreement, the significant assistance quantum chemical calculations can offer in the assignment of ^{13}C NMR spectra can be demonstrated. Experimental and theoretical values of the ^{13}C NMR spectra for (*Z*)-CPMPE **2** and (*Z*)-CBMPE **1** have been compiled in Table 3. In the spectrum of (*Z*)-CPMPE **2**, only two signals can be readily assigned from the experimental data alone: the methoxy carbon C(10A) at 55.64 ppm and the methoxy-bearing C(2A) at 157.97 ppm. Two signals in the spectrum, at 128.97 and 126.08 ppm, have a conspicuously higher intensity than the others and must be attributed to the pairs of equivalent carbon atoms C(2B)/C(6B) and C(3B)/C(5B), but it is impossible to distinguish them. Both the HF and the DFT calculations, however, assign the downfield peak to C(3B)/C(5B). As a further set of reference points, the other quarternary carbon atoms are predicted in the correct place by the HF calculation; DFT switches C(3A) and C(7), and C(1B) and C(8)—we note that the chemical shift difference between the latter two is very small (0.2 ppm). For (*Z*)-CBMPE **2**, the HF shifts agree perfectly with the observed quaternary carbons, while there are discrepancies in the results of the DFT calculations. Comparison of the chemical shifts of the A-ring with those of (*Z*)-CPMPE **2** indicates that the assignment of C(6A), which is wrong in HF, is correct in DFT. The differences between calculated and experimental shifts are attributable to solvatation and conformational effects. The assignments of C(1B) and C(4B), and of C(3B) and C(3A) remain open to discussion.

Table 1 Calculated (HF and DFT) energy differences ΔE and ΔG between the lowest energy conformers of the *cis*- and *trans*-isomers in kJ mol^{-1} and theoretical and experimental fractions of *cis* at the thermodynamic equilibrium (see text for details)

	ΔE (HF)	ΔE (DFT)	ΔG (DFT)	Obs
CBMPE	1.38	6.78	6.32	—
CPMPE	5.56	11.72	—	—
BMPE	13.97	18.49	20.00	—
		%*cis*	%*cis*	%*cis*
CBMPE	—	13.8	15.7	11.2
CPMPE	—	3.3	—	4.4
BMPE	—	0.4	0.3	0.5

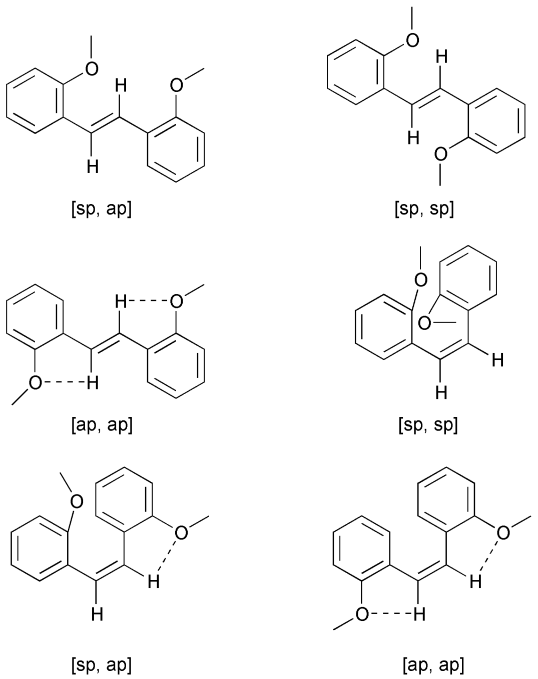

Fig. 4 Possible conformations for the *E*-(top) and *Z*-configurations (bottom) of BMPE **3**. Planar forms are drawn for simplicity.

Table 2 Selected geometrical parameters for (*Z*)-CBMPE **1**, (*Z*)-CPMPE **2**, (*E*)-BMPE **3** and (*E*)-stilbene. Calculated (DFT, r_e distances in Å and angles in °) and solid-state results (XRD, bond lengths in Å and angles in °)

		(*Z*)-CBMPE **1**	(*Z*)-CPMPE **2**	(*E*)-BMPE **3**[a]	(*E*)-Stilbene[c]
XRD	C(7)–C(8)	1.353(3)	1.347(4)	1.320(4)	1.326(2)
	C(1A)–C(8)	1.458(3)	1.459(4)	1.454(4)	1.471(2)
	C(1B)–C(7)	1.487(3)	1.485(4)	1.461(4)	1.471(2)
	C(11)–N(12)	1.143(4)	1.144(3)	—	—
	C(7)–C(11)	1.436(4)	1.428(4)	—	—
	CH–*n*(O)	2.429	2.315	2.355[b]	—
	C(2A)–C(1A)–C(8)–C(7)	−143.2(3)	−161.1(3)	−165.0(3)	−184[d]
	C(2B)–C(1B)–C(7)–C(8)	−140.3(2)	−153.8(4)	−177.3(3)	−176[d]
DFT	C(7)–C(8)	1.362	1.363	1.350	1.348
	C(1A)–C(8)	1.460	1.458	1.465	1.466
	C(1B)–C(7)	1.491	1.489	1.465	1.466
	C(11)–N(12)	1.165	1.165	—	—
	C(7)–C(11)	1.435	1.434	—	—
	CH–*n*(O)	2.260	2.256	2.341	—
	C(2A)–C(1A)–C(8)–C(7)	165.6	164.6	−163.0	−176.8
	C(2B)–C(1B)–C(7)–C(8)	133.6	152.5	−163.0	−176.8

[a] See ref. 37. [b] The molecule is asymmetric in the solid; the corresponding value for the other ring is 2.350 Å. [c] See ref. 38. [d] (*E*)-Stilbene has two different (symmetric) stilbene molecules in the asymetric unit. Their respective values for the torsion angles are −175.0(2)° at the A-site and −176.1(2)° at the B-site. At the B-site, disorder can occur, and B is substituted for a B′-molecule with a torsion angle of 174.3(8)°. The bond lengths are nearly identical, and shown here for the A molecule.[38]

Table 3 Experimental (δ) and calculated (HF and DFT) ^{13}C chemical shifts (ppm) with reference to TMS for (*Z*)-CBMPE **1** and (*Z*)-CPMPE **2** (see text for details); *q* designates a quarternary carbon atom

	Experimental			Calculated			
		δ		δ(HF)		δ(DFT)	
(*Z*)-CPMPE **2**	C(2A)	157.97	q	157.62	C(2A)	153.63	C(2A)
	C(8)	137.47		142.58	C(8)	134.41	C(1B)
	C(1B)	134.88	q	137.12	C(1B)	134.21	C(8)
	C(4A)	131.94		135.08	C(4A)	126.92	C(4A)
	C(3B),C(5B)	128.97		134.09	C(6A)	125.22	C(6A)
	C(6A)	128.94		127.79	C(3B),C(5B)	123.53	C(3B),C(5B)
	C(4B)	128.56		127.04	C(4B)	122.85	C(4B)
	C(2B),C(6B)	126.08		126.16	C(2B),C(6B)	121.85	C(2B),C(6B)
	C(1A)	123.15	q	119.73	C(1A)	120.23	C(1A)
	C(5A)	120.84		117.15	C(5A)	115.68	C(5A)
	C(11)	118.19	q	113.69	C(11)	111.67	C(11)
	C(7)	111.70	q	106.25	C(3A)	106.89	C(7)
	C(3A)	110.80		105.66	C(7)	103.85	C(3A)
	C(10A)	55.64		50.32	C(10A)	53.64	C(10A)
(*Z*)-CBMPE **1**	C(2A)	157.79	q	157.31	C(2A)	152.15	C(2A)
	C(2B)	157.13	q	156.08	C(2B)	152.02	C(2B)
	C(8)	141.34		144.31	C(8)	136.51	C(8)
	C(4A)	131.62		134.46	C(4A)	126.78	C(4A)
	C(6B)	130.29		134.10	C(6A)	126.38	C(6B)
	C(4B)	130.06		133.54	C(6B)	125.93	C(1B)
	C(6A)	128.64		131.20	C(4B)	125.50	C(6A)
	C(1B)	125.10	q	126.81	C(1B)	125.15	C(4B)
	C(1A)	123.47	q	120.26	C(1A)	120.60	C(1A)
	C(5B)	120.98		117.43	C(5B)	115.35	C(5A)
	C(5A)	120.76		117.13	C(5A)	114.55	C(5B)
	C(11)	118.26	q	112.52	C(11)	110.10	C(11)
	C(3B)	111.61		107.78	C(3B)	105.99	C(7)
	C(3A)	110.74		106.07	C(3A)	105.20	C(3B)
	C(7)	109.05	q	105.73	C(7)	104.17	C(3A)
	C(10A)	55.79		50.20	C(10A)	54.06	C(10A)
	C(10B)	55.61		50.04	C(10B)	53.77	C(10B)

Isomerisation experiments

The isomerisation process was studied by means of gas chromatography with a flame ionisation detector (FID), since the FID yields a quantitative signal, unperturbed by differences in absorption or emission wavelength and absorption coefficient, which would be the case if a UV detector was used. The isomer with the phenyl groups *trans* on the double bond is in all three cases accessible because it is formed in excess in the reactions used, and can be crystallised from of the mixture of isomers. For BMPE **3** in the Wadsworth–Emmons reaction, however, the *E*-isomer is formed exclusively. To unequivocally determine the precise configuration of the crystalline fraction of these trisubstituted ethylenes, we solved the crystal structures of CBMPE **1** and CPMPE **2** by X-ray diffraction. This confirmed the presence of the *Z*-isomers of both compounds in the crystal.

Thermal isomerisations were performed on the compounds under investigation using a trace amount of iodine. These types of isomerisations are ground-state chemical processes, yielding the thermodynamic equilibrium between the ground-state geometries.[31] Table 1 contains the experimentally determined fractions of the *cis*-isomer in the equilibrium mixtures and compares them to the calculated values, both determined from the 0 K energy *E* and the Gibbs free energy *G* (see above). The theoretical values agree quite well with the experimental values. All of this is in striking contrast with what happens when a dilute solution of the compounds is exposed to UV-light.

The photochemical isomerisation procedure used here is not standard,[32–34,35] but gives, in a reproducible way, the photochemical equilibrium that is reached in daylight in normal transparant glassware. It also sheds light on the speed with which the isomerisation takes place under these conditions, which is of the utmost importance when it comes to knowing how careful one needs to be with shielding solutions from light when compounds are being processed for various applications. The emission peak of the lamp used in the experiments has a broad maximum at 365 nm and is thus non-monochromatic. It is sufficiently broad for the three compounds employed in this study to be irradiated with approximately the same amount of energy at and around their absorption maxima (329–337 nm).

Table 4 Results of the photochemical isomerisation experiments: composition of isomer mixture at photochemical equilibrium and time $t_{1/2}$ (min) to 50 : 50 mixture are given (see text for details)

	%*cis*	%*trans*	$t_{1/2}$
CBMPE	83	17	175
CPMPE	85	15	270
BMPE	91	9	226

The experiments showed that the isomer composition stayed the same when the lamp was out, and also whenever a break from constant irradiation was taken. GC–MS was used to corroborate that the isomerisation process was not a photochemical breakdown or cyclisation process. The results of these experiments are presented in Table 4: $t_{1/2}$ is the time the mixture needed to reach the 50 : 50 mixture of isomers and the final values for the composition of the isomer mixture are those measured after 1000 min (16 h 40 min) of irradiation. At this point changes in the composition of the mixture were negligible. The obvious conclusion from Table 4 is that these experimental values differ vastly from the ones obtained in the thermodynamic isomerisation and consequently from those calculated. It appears that for these stilbene derivatives, the ground state relative energies are sufficiently different from the excited state relative energies of the isomers for the outcome of the isomerisation process to be completely different. Consequently, in contrast with the analogous 1,2-di-2-thienylethenes, for these stilbenes, a description of substituent effects in the ground state does not explain the composition of the equilibrium mixture after a photochemical isomerisation (an excited state process). A theoretical description must therefore come from calculations of the excited states and these are currently underway.

Crystal structure and substituent effects

The following concentrates on the geometrical features that were found to be of major importance in the determination of the isomerisational behaviour of the corresponding 1,2-di-2-thienylethenes.[7] Experimental and theoretical values for these geometrical parameters have been presented in Table 2.

A striking difference appears in the crystal packing of (*Z*)-CBMPE **1** and (*Z*)-CPMPE **2**, which may have repercussions on their performance in thin film applications. The intramolecular effects, discussed later, clearly show their influence at this point. The packing of the cell for (*Z*)-CPMPE **2** is straightforward: the molecules are stacked so that the B-ring and the =C–CN fragment lie in more or less parallel layers, while the methoxy substituted phenyl rings are twisted out so that all the methoxy groups are located in another plane. This results in a sandwiched structure, clearly shown in the projections in Fig. 5, which nevertheless retains conjugation and the CH–*n*(O) interactions. The crystal structure of (*Z*)-CBMPE **1**, of which two projections are shown in Fig. 6, shows the two phenyl rings being positioned perpendicular to each other. In the absence of stabilising interactions from surrounding molecules, a stacking similar to the one found for (*Z*)-CPMPE **2** (with the B-ring/=C–CN residues on the one hand and the methoxy groups on the other clearly grouped together), is no longer possible due to the disturbance introduced by the increased number of methoxy groups. The crystal structure can only be stabilised by stacking the aromatic rings on top of each other by twisting the A-ring further away from the plane of the spacer. Loss of conjugation and the weakening of the CH–*n*(O) interactions results.

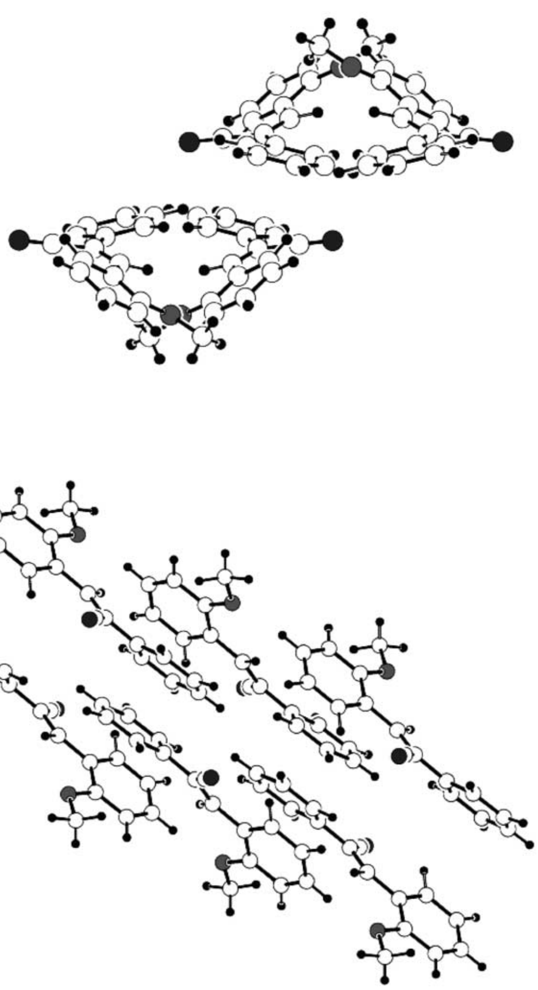

Fig. 5 A view of the packing of molecules of (*Z*)-CPMPE **2** along the *c*-axis (top) and the *b*-axis (bottom).[39]

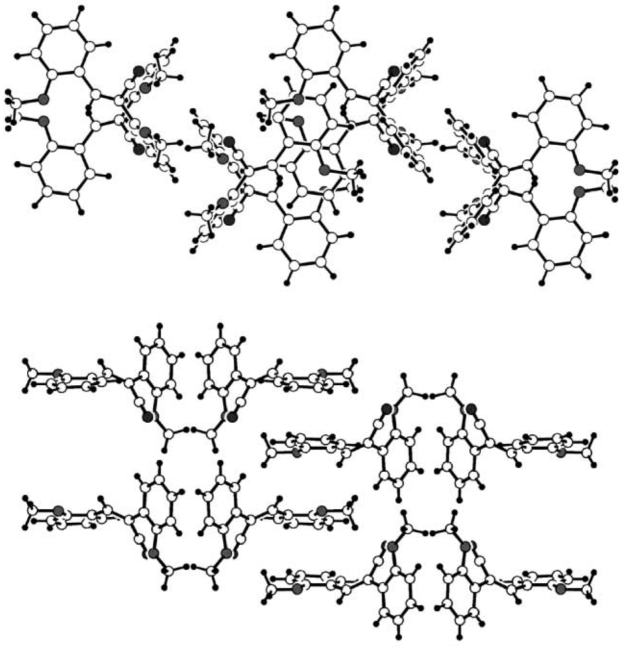

Fig. 6 A view of the packing of molecules of (*Z*)-CBMPE **1** along the *b*-axis (top) and the *a*-axis (bottom).[39]

In all three compounds, the methoxy group on the A-ring, next to H(8) on the double bond, makes a CH–*n*(O) interaction possible and this results in considerably shorter H–O distances: as can be seen from Table 2 the distances lie well below the sum of the Van der Waals radii (2.72 Å). Thus the methoxy substituted rings do not twist out of the plane as far as would be expected from a steric viewpoint. The B-rings of (*Z*)-CPMPE **2** and (*Z*)-CBMPE **1** are only kept in the plane through the stabilising conjugation with the rest of the π-system. Additional differences can be attributed to steric interactions, which affect the B-ring in (*Z*)-CBMPE **1** more, since it is bearing an additional methoxy group. In the crystal, the B-ring methoxy group in (*Z*)-CBMPE **1** faces the nitrile group, which may indicate an attractive interaction between C(11) and O(9B). The fact that only the calculated lowest energy conformer is found in the solid phase is due to stabilising stacking effects.

In the list of bond lengths in Table 2 no unexpected effects are found: due to the electronwithdrawing effect of the nitrile moiety both the ethenylic bond C(7)–C(8) and C(7)–C(1B) have become longer in the nitrile substituted compounds, when compared to the corresponding bonds in (*E*)-BMPE **3** and stilbene. The effect on the single bond on the far side of the ethenylic link, C(7)–C(1A), is almost negligible. While the length of the C(11)–N(12) bond in (*Z*)-CBMPE **1** and (*Z*)-CPMPE **2** is identical, both in the gas phase and the solid state, the bond lengths C(11)–C(7) and C(7)–C(8), which also show up as nearly identical in the calculations, are both slightly longer in (*Z*)-CBMPE **1**.

The apparent effects of the conformations in the UV spectra are equally interesting. From measurements[7] and calculations[36] on the thienyl analogues it is known that the latter are planar, resulting in their effective conjugation lengths being more or less the same. If we look at the absorption maxima for the phenyl analogues, we find that (*E*)-BMPE **3**, which has the most planar structure (17.0° torsion angle in the gas phase), has a λ_{max} of 329 nm. Starting from the increments observed for the thiophenes, we would expect for (*Z*)-CPMPE **2** to have a λ_{max} of 349 nm and (*Z*)-CBMPE **1** one of 356 nm. The smaller observed values must be due to deplanarisation of the molecules (through twisting of the phenyl rings from the plane of the vinyl spacer), reducing the size of the resonance space and lowering the value of λ_{max}. For (*Z*)-CPMPE **2** with the B-ring making an angle of about 26° with the spacer, the effect is smaller (12 nm) than for (*Z*)-CBMPE **1**, where the loss of conjugation and associated shift of λ_{max} is very apparent (26 nm). The B-ring makes an angle of 46°.

XRD data point in the same direction: while (*E*)-BMPE **3** is almost completely planar,[37] the other two compounds show the outer rings at a significantly larger angle with the plane of the double bond, as can be seen from Table 2.

Conclusion

For the three substituted stilbenes, the ground state approach to predict the photochemical isomerisation equilibria, based on calculated energy difference, does not hold as well as it does for the studied thienyl analogues. On the other hand, the thermodynamic equilibria of the compounds in question can be reproduced satisfactorily. Additionally, the same structural features that were responsible for the behaviour of the thienyl compounds, play a role in the conformations of these molecules, although deplanarisation is more frequent and larger for the stilbenes, due to more prominent steric effects.

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