ORIGINAL PAPER

# Kinetically stable high-energy isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ derived from *cis*-stilbene and *cis*-azobenzene

**Jon Baker · Krzysztof Wolinski**

**Abstract** Following on from our recent enforced geometry optimization (EGO) investigation of isomerization in *cis*-stilbene (*J Comput Chem*, in press) we report the discovery of two interesting new, symmetrical "fused sandwich" isomers of both *cis*-stilbene and the related *cis*-azobenzene. The isomers were obtained by applying external forces to pairs of carbon atoms from each of the benzene rings in *cis*-stilbene and *cis*-azobenzene simultaneously, and are all at least 100 kcal mol$^{-1}$ higher in energy than the starting material. Each new structure was characterized as a minimum by vibrational analysis. Despite their high energy, all of the new isomers appear to be kinetically stable with respect to rearrangement back to *cis*-stilbene or *cis*-azobenzene, respectively.

**Keywords** Enforced geometry optimization · Symmetrical "fused sandwich" isomers

## Introduction

In previous publications we reported the discovery of several potentially kinetically stable new isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ derived from *cis*-stilbene (1) [1]

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and *cis*-azobenzene (2) [2] (see Fig. 1), respectively. They were obtained using enforced geometry optimization (EGO), in which pairs of carbon atoms, one from each of the two phenyl rings, were pushed together along the line joining the two atomic centers, by means of an applied external force [3]. This force is added to the normal gradient vector computed at that geometry at each cycle of a geometry optimization and typically results in bond formation between the atoms involved. All atoms in the system adjust their relative positions so as to counter the external force and the final result of the optimization is usually a new structure, albeit one that is highly strained. Whether the new structure is stable, i.e., represents a local minimum on the potential energy surface, can be determined by carefully reoptimizing with the external force removed. If the new structure is stable, it will relax but remain substantially intact; if not it usually reverts back to the starting structure.

All the kinetically stable isomers found in our earlier work were obtained by forcing together only a single pair of carbon atoms and all lay energetically no higher than 90 kcal mol$^{-1}$ from the starting material for the stilbene isomers, and under 30 kcal mol$^{-1}$ in the case of *cis*-azobenzene. In this communication we report the discovery of some interesting high-energy symmetric "fused sandwich" isomers of both stilbene and azobenzene obtained by forcing together multiple pairs of carbon atoms (in this case all six) from each of the two phenyl rings.

## Results and discussion

The standard methodology used in this work is density functional theory (DFT) [4, 5] using the B3LYP hybrid
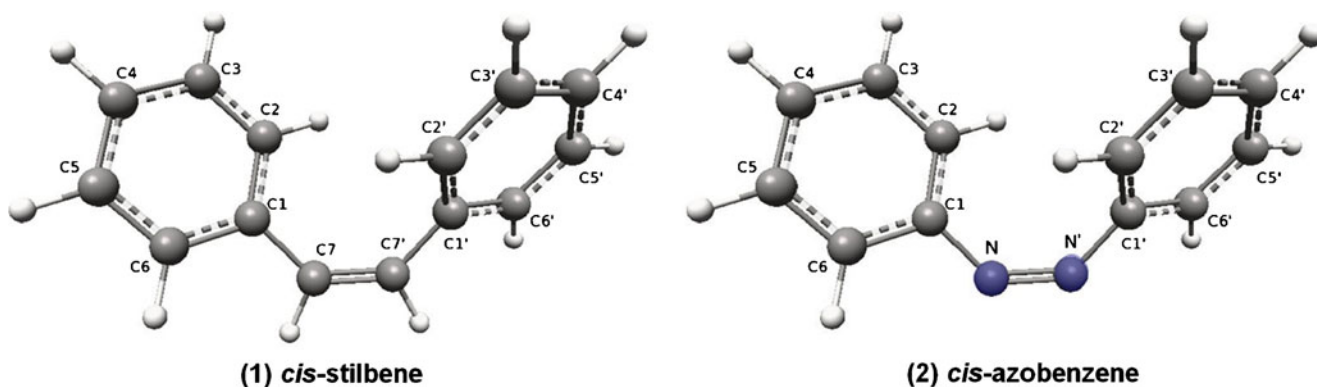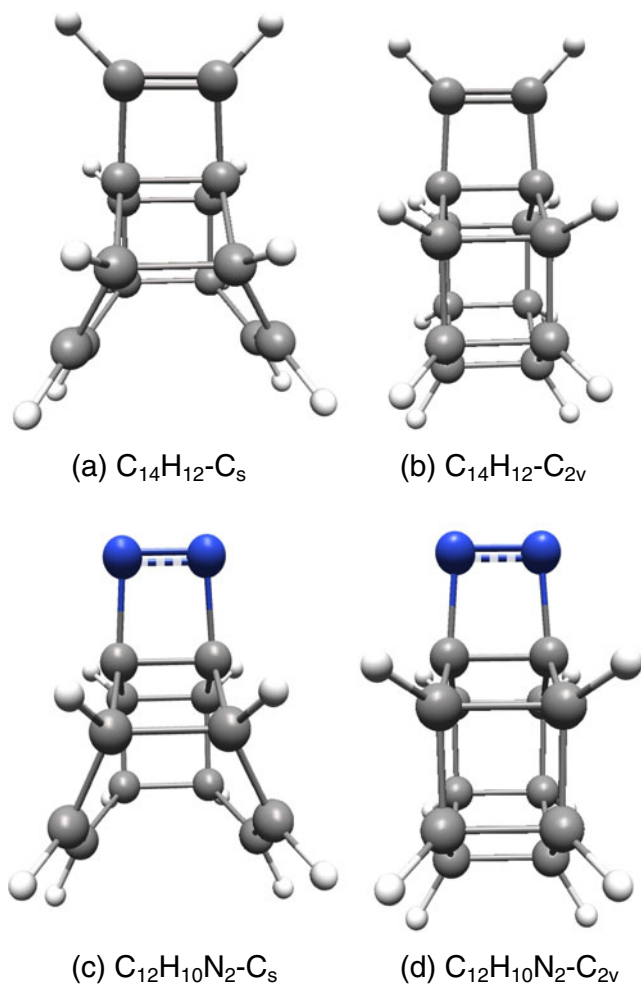
**Fig. 1** Schematic showing structure and atom labeling of *cis*-stilbene (**1**) and *cis*-azobenzene (**2**)

exchange-correlation functional [6, 7] with the 6-31G* basis set [8]. All calculations were carried out using the *PQS* program package incorporating the *PQSMol* graphical user interface for post-job visualization and display [9]. All



(a) $C_{14}H_{12}$-$C_s$   (b) $C_{14}H_{12}$-$C_{2v}$

(c) $C_{12}H_{10}N_2$-$C_s$   (d) $C_{12}H_{10}N_2$-$C_{2v}$

**Fig. 2** High energy isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ obtained via an enforced geometry optimization by pushing together all symmetry related pairs of carbon atoms in the phenyl rings of *cis*-stilbene and *cis*-azobenzene, respectively

stationary points found at B3LYP/6-31G* were reoptimized at MP2/6-311G** to ensure that the energetics remained stable.

The new isomers, which we call $C_{14}H_{12}$-$C_s$, $C_{14}H_{12}$-$C_{2v}$, $C_{12}H_{10}N_2$-$C_s$ and $C_{12}H_{10}N_2$-$C_{2v}$ are shown in Fig. 2. They were all obtained by pushing together all symmetry equivalent pairs of carbon atoms from the two phenyl rings in *cis*-stilbene and *cis*-azobenzene, respectively. As denoted by the names, the new isomers have either $C_s$ or $C_{2v}$ symmetry. The optimization history for this procedure starting from *cis*-stilbene using an applied force of 0.1 au is depicted in Scheme 1, below.
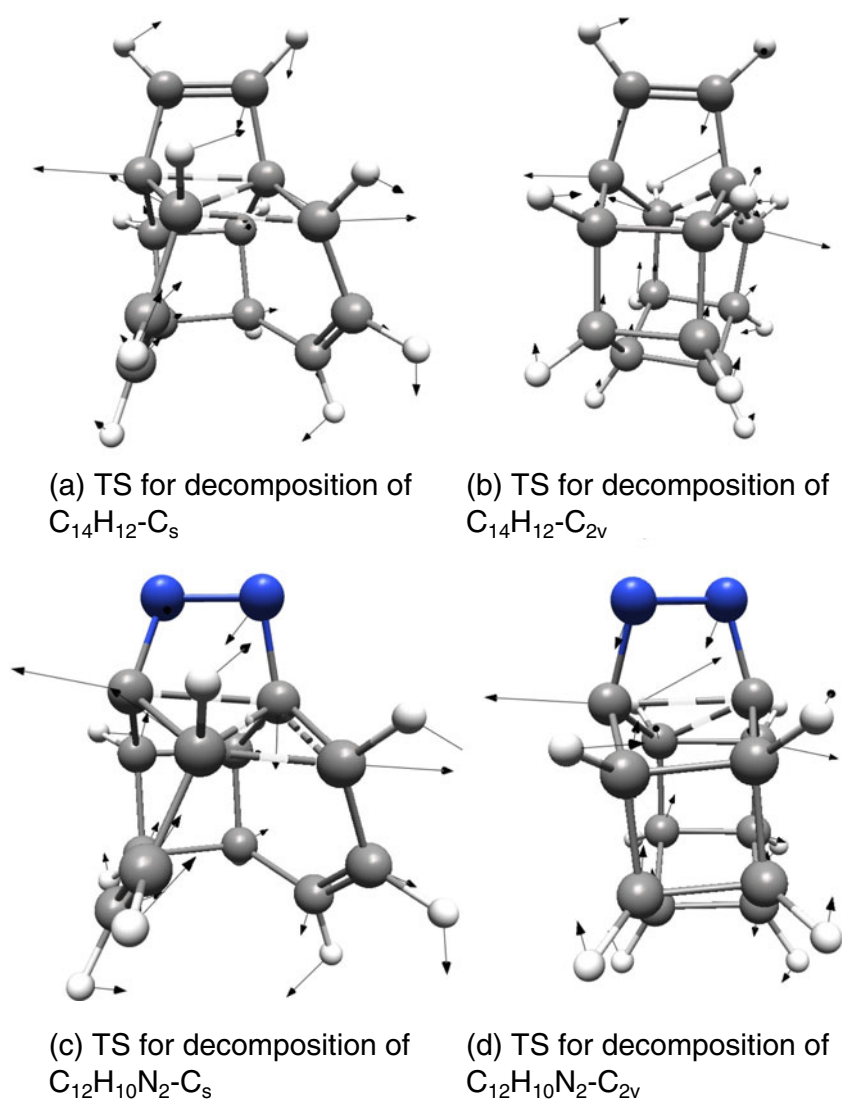
As can be seen, the energy initially rises to a maximum, then falls and then starts to oscillate. The calculation did not in fact converge, but simply stopped after reaching the maximum allowed number of optimization cycles. Apparently there is simply too much internal strain in the system for it to settle down. If the geometry corresponding to the highest energy oscillation is taken and allowed to relax (i.e., is reoptimized after removing the external force) then the $C_{2v}$ minimum results; if the lower energy structure is relaxed then the result is the $C_s$ minimum. The situation is similar for *cis*-azobenzene.

As shown in Fig. 2 the new isomers are symmetrical "fused sandwich" compounds in which the former phenyl rings lay one on top of the other (or side-by-side depending on one's point of view). In the $C_{2v}$ isomers, every carbon atom in each of the phenyl rings forms a bond to its



**(1) EGO optimization history**
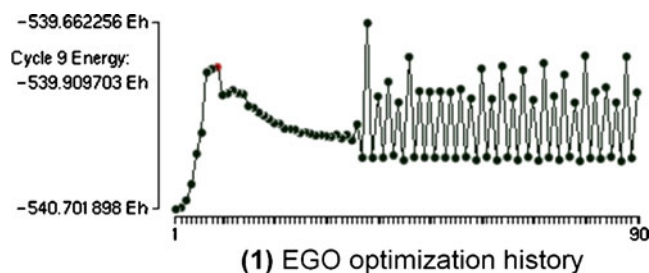
**Scheme 1** EGO optimization history

Fig. 3 Transition states for decomposition of the new $C_s$ and $C_{2v}$ isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$, respectively, together with arrows showing the motion of the atoms in the imaginary vibrational mode



(a) TS for decomposition of $C_{14}H_{12}$-$C_s$

(b) TS for decomposition of $C_{14}H_{12}$-$C_{2v}$

(c) TS for decomposition of $C_{12}H_{10}N_2$-$C_s$

(d) TS for decomposition of $C_{12}H_{10}N_2$-$C_{2v}$

equivalent atom in the other ring. In the $C_s$ isomers, two of the carbon atoms in each phenyl ring open out and are not bonded to the two equivalent atoms in the other ring. If – as is the case in Fig. 2 – the former ethylene fragment in cis-stilbene and the N=N double bond in azobenzene are oriented so they are at the top of each isomer, then in the $C_s$ isomer the carbon atom at the apex of the former phenyl ring at the bottom is not bonded, together with one of the

Table 1 Selected B3LYP/6-31G* distances (Å) in the new isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ and their transition states

| | C7=C7′ | C1-C1′ | C2-C2′ | C3-C3′ | C4-C4′ | C5-C5′ | C6-C6′ |
|---|---|---|---|---|---|---|---|
| $C_{14}H_{12}$-$C_s$ | 1.351 | 1.543 | 1.576 | 1.601 | 3.000 | 2.986 | 1.622 |
| $C_{2v}$ TS | 1.350 | 1.553 | 1.568 | 2.262 | 2.962 | 2.262 | 1.568 |
| $C_1$ TS | 1.355 | 1.961 | 1.556 | 1.595 | 2.899 | 2.999 | 1.963 |
| $C_{14}H_{12}$-$C_{2v}$ | 1.349 | 1.557 | 1.585 | 1.559 | 1.568 | 1.559 | 1.585 |
| $C_1$ TS | 1.353 | 2.046 | 1.569 | 1.561 | 1.567 | 1.565 | 1.703 |
| | N=N | C1-C1′ | C2-C2′ | C3-C3′ | C4-C4′ | C5-C5′ | C6-C6′ |
| $C_{12}H_{10}N_2$-$C_s$ | 1.279 | 1.498 | 1.586 | 1.602 | 3.002 | 2.993 | 1.633 |
| $C_{2v}$ TS | 1.279 | 1.505 | 1.577 | 2.266 | 2.964 | 2.266 | 1.577 |
| $C_1$ TS | 1.330 | 2.008 | 1.554 | 1.602 | 2.959 | 2.988 | 1.767 |
| $C_{12}H_{10}N_2$-$C_{2v}$ | 1.278 | 1.511 | 1.597 | 1.559 | 1.568 | 1.559 | 1.597 |
| $C_1$ TS | 1.328 | 2.007 | 1.564 | 1.563 | 1.568 | 1.567 | 1.628 |

**Table 2** Energies of the new isomers of $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ and their transition states relative to cis-stilbene and cis-azobenzene, respectively

[a] kcal mol$^{-1}$ relative to cis-stilbene; [b] kcal mol$^{-1}$ relative to cis-azobenzene

| Structure | B3LYP[a]6-31G* | MP2[a]6-311G** | Structure | B3LYP[b]6-31G* | MP2[b]6-311G** |
|---|---|---|---|---|---|
| $C_{14}H_{12}$-$C_s$ | 125.1 | 104.8 | $C_{12}H_{10}N_2$-$C_s$ | 117.3 | 99.3 |
| $C_{2v}$ TS | 151.9 | 127.3 | $C_{2v}$ TS | 144.3 | 122.0 |
| $C_1$ TS | 163.8 | 138.1 | $C_1$ TS | 146.2 | 120.2 |
| $C_{14}H_{12}$-$C_{2v}$ | 170.4 | 150.9 | $C_{12}H_{10}N_2$-$C_{2v}$ | 161.1 | 143.6 |
| $C_1$ TS | 205.7 | 181.7 | $C_1$ TS | 190.2 | 166.1 |

two carbon atoms connected to the apex carbon. In fact, there are two symmetry-equivalent $C_s$ structures depending on which of the two carbon atoms either side of the apex atom are bonded with a $C_{2v}$ transition state connecting the two equivalent $C_s$ isomers.

We have located $C_1$ structures which appear to be transition states for decomposition of the $C_s$ and $C_{2v}$ isomers, respectivel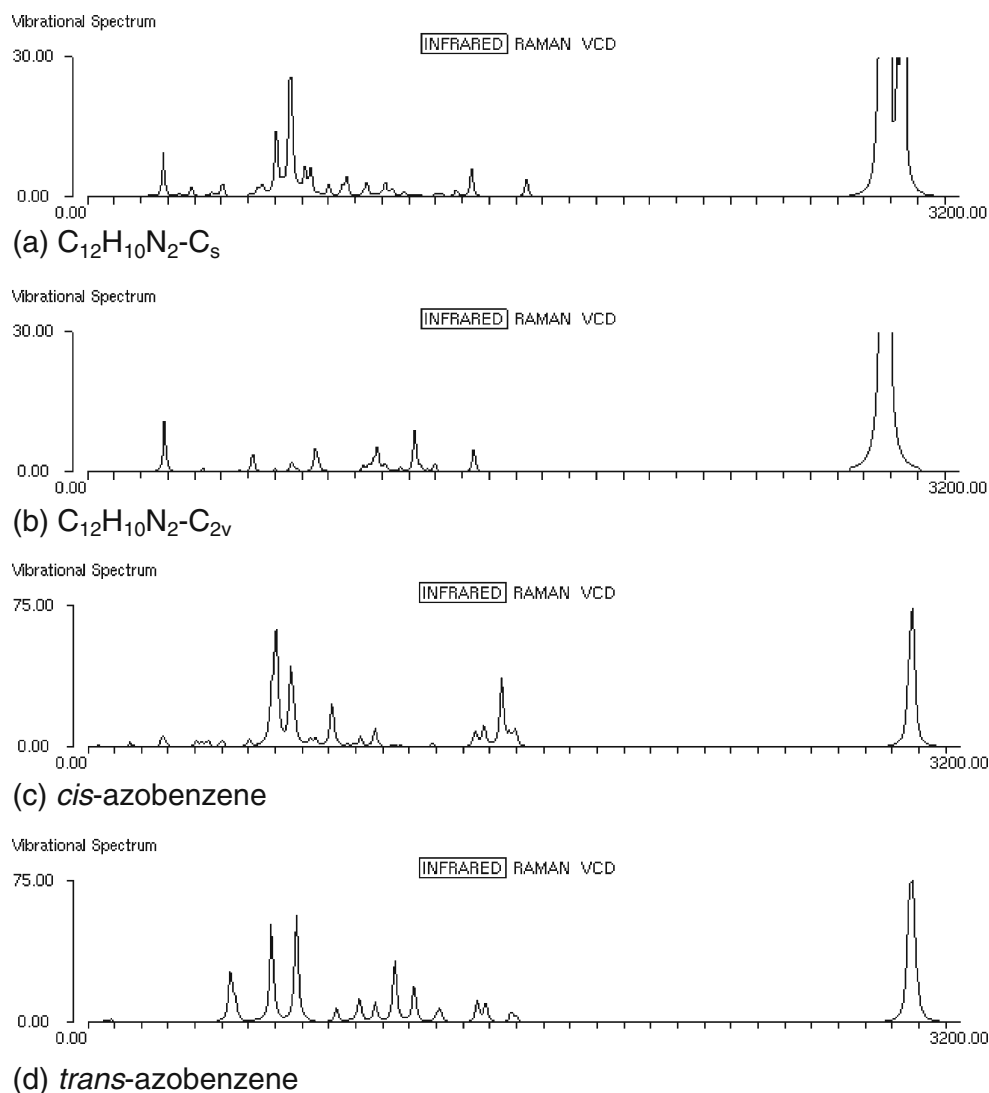y, back to either cis-stilbene or cis-azobenzene. These are depicted in Fig. 3, together with arrows showing the motion of the atoms in the imaginary vibrational mode.

Selected B3LYP/6-31G* geometrical parameters (primarily the inter-ring C-C distances) in all stationary points (four minima and six transition states) are shown in Table 1 and relative energies of all species at both B3LYP/6-31G* and MP2/6-311G** are given in Table 2. All energies are relative

**Fig. 4** Simulated SQM-scaled B3LYP/6-31G* IR spectra of $C_{14}H_{12}$-$C_s$, $C_{14}H_{12}$-$C_{2v}$, and cis- and trans-stilbene



(a) $C_{14}H_{12}$-$C_s$

(b) $C_{14}H_{12}$-$C_{2v}$

(c) cis-stilbene
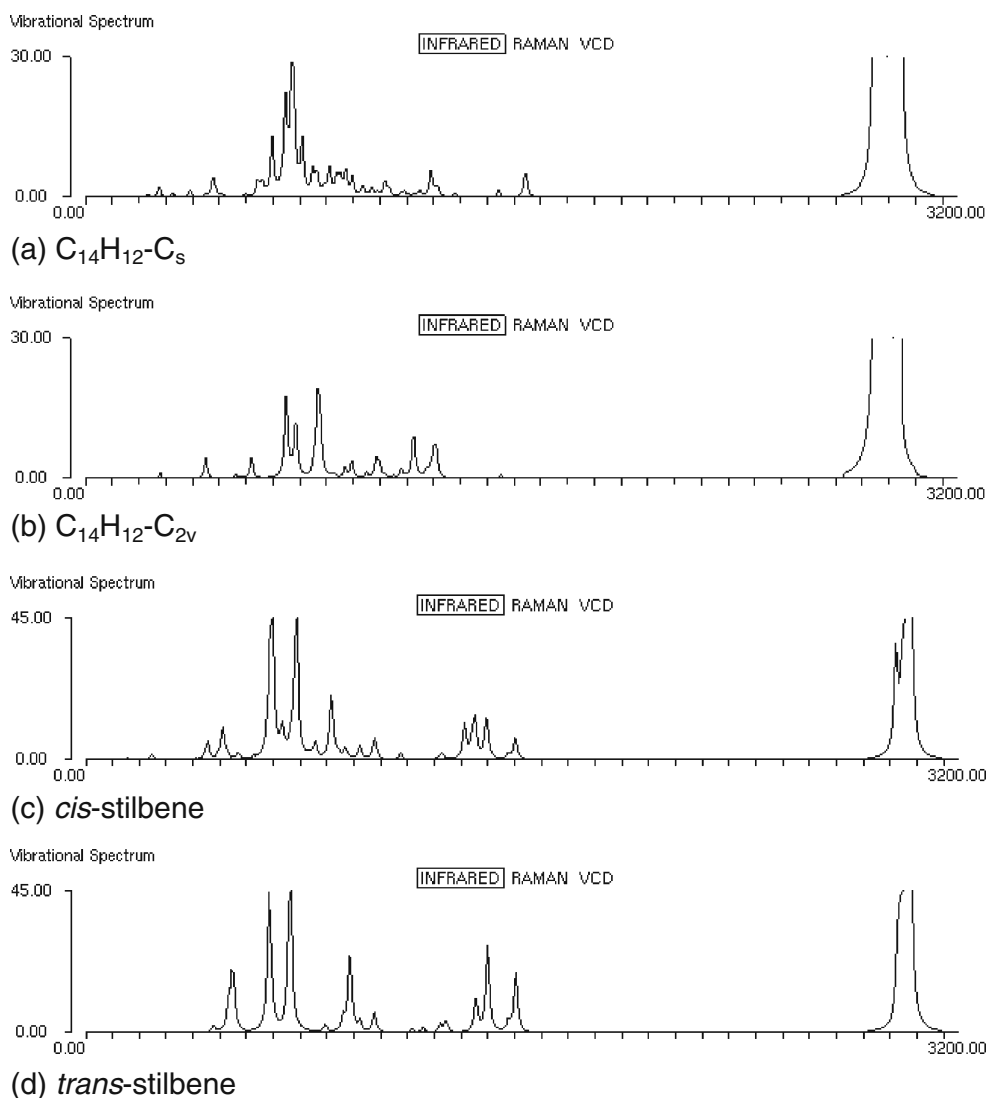
(d) trans-stilbene

Fig. 5 Simulated SQM-scaled B3LYP/6-31G* IR spectra of $C_{12}H_{10}N_2$-$C_s$, $C_{12}H_{10}N_2$-$C_{2v}$ and *cis*- and *trans*-azobenzene



(a) $C_{12}H_{10}N_2$-$C_s$

(b) $C_{12}H_{10}N_2$-$C_{2v}$

(c) *cis*-azobenzene

(d) *trans*-azobenzene

to either *cis*-stilbene or *cis*-azobenzene as appropriate. The atom labeling used in Table 1 is shown in Fig. 1. External forces were applied between each pair of primed and unprimed carbon atoms labeled 1 through 6. In the $C_{2v}$ minima a new bond was formed between all primed and unprimed carbon atoms; in the $C_s$ minima bonds were formed between primed and unprimed carbon atoms 1, 2, 6 and either 3 or 5 (leading to the two symmetry-related $C_s$ isomers). The labeling in *cis*-azobenzene is the same, except that N replaces C7.

Both structurally (Table 1; Figs. 2 and 3) and energetically (Table 2) the new $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ isomers and their transition states are similar to one another. In particular both the $C_s$ and $C_{2v}$ minima appear to be kinetically stable, with barriers to decomposition (B3LYP/6-31G* with MP2/6-311G** values in parentheses) of 38.7 (33.3) kcal mol$^{-1}$ for $C_{14}H_{12}$-$C_s$, 24.0 (30.8) kcal mol$^{-1}$ for $C_{14}H_{12}$-$C_{2v}$, 28.9 (20.9) kcal mol$^{-1}$ for $C_{12}H_{10}N_2$-$C_s$ and 29.1 (22.5) kcal mol$^{-1}$

for $C_{12}H_{10}N_2$-$C_{2v}$. The barrier heights for the $C_s$-$C_s$ rearrangement are 26.8 (22.5) kcal mol$^{-1}$ for $C_{14}H_{12}$-$C_s$ and 27.0 (22.7) kcal mol$^{-1}$ for $C_{12}H_{10}N_2$-$C_s$. All quoted values are well-to-well and exclude zero-point effects. As was the case with the other recently reported $C_{14}H_{12}$ and $C_{12}H_{10}N_2$ isomers [1, 2], nearly all structures are predicted to be more stable thermodynamically but less stable kinetically at the MP2 level than with B3LYP.

The simulated IR and Raman spectra for the four new "fused sandwich" isomers reported here, together with those for *cis*- and *trans*-stilbene and ditto azobenzene, are shown in Figs. 4, 5, 6, 7. These were obtained directly from the computed B3LYP/6-31G* force constant (Hessian) matrix, scaled using the five standard precomputed scaled quantum mechanical (SQM) scale factors [10] shown in Table 3, and visualized using the *PQSMol* graphical user interface available with *PQS* [9]. All spectra have been partially standardized to aid comparison.

**Fig. 6** Simulated SQM-scaled B3LYP/6-31G* Raman spectra of $C_{14}H_{12}$-$C_s$, $C_{14}H_{12}$-$C_{2v}$ and *cis*- and *trans*-stilbene



(a) $C_{14}H_{12}$-$C_s$

(b) $C_{14}H_{12}$-$C_{2v}$

(c) *cis*-stilbene

(d) *trans*-stilbene
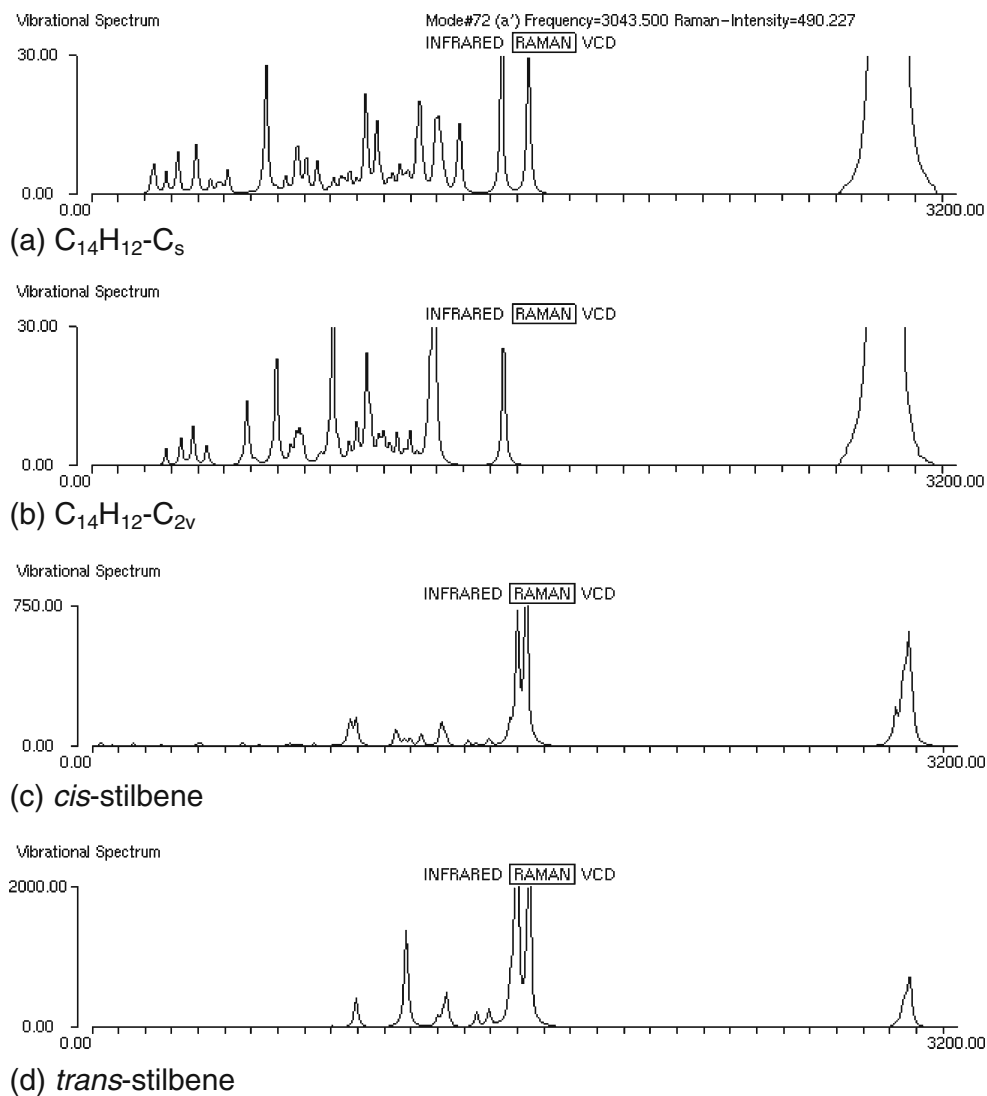
Both the IR and Raman spectra of the four new isomers are dominated by intense bands in the C-H stretching region. These are predicted to be so intense relative to any of the other bands (by a factor of more than 5 in the IR and 20 in the Raman) that the intensity scale has been reduced in order to show detail in the fingerprint region.

For the Raman spectra in particular, although the new high-energy isomers have richer spectra with more bands than the parent compounds (stilbene and azobenzene), the bands in the latter are far more intense (note the intensity scales in Figs. 6 and 7); this, combined with their likely far greater concentration in any mixture containing the new isomers – unless they can somehow be isolated – suggests than Raman spectroscopy is unlikely to be a viable method for detecting the proposed new species. The same holds, albeit to a lesser extent, for IR spectroscopy.

A potentially more useful approach as far as detection is concerned may be NMR. Table 4 gives the (absolute) B3LYP/

6-31G* $^{13}$C and $^{1}$H chemical shifts computed for *cis*- and *trans*-stilbene, $C_{14}H_{12}$-$C_s$ and $C_{14}H_{12}$-$C_{2v}$, and Table 5 reports the same for the corresponding azo compounds. As can be seen there are substantial shifts upfield (averaging about 90 ppm) on all phenyl carbon nuclei in the $C_{2v}$ isomer and on two thirds of them in the $C_s$ isomer. (Basically every carbon atom involved in bond formation is shifted upfield.) The carbon atoms in the formal ethylenic C=C double bond shift downfield compared to *cis*-stilbene by about 15 ppm. The situation in the azo compounds is similar with again any phenyl carbon atom forming a new bond shifted upfield by around 90 ppm and the $^{15}$N signal shifting downfield relative to *cis*-azobenzene by about 70 ppm.

The effect of bond formation can also be seen in the proton chemical shifts, with any hydrogen attached to a bonding phenyl carbon shifting upfield by around 4 ppm. The fact that these shifts are substantial and are uncontaminated in this region of the NMR spectrum by any signals

**Fig. 7** Simulated SQM-scaled B3LYP/6-31G* Raman spectra of $C_{12}H_{10}N_2$-$C_s$, $C_{12}H_{10}N_2$-$C_{2v}$ and *cis*- and *trans*-azobenzene



(a) $C_{12}H_{10}N_2$-$C_s$

(b) $C_{12}H_{10}N_2$-$C_{2v}$

(c) *cis*-azobenzene

(d) *trans*-azobenzene
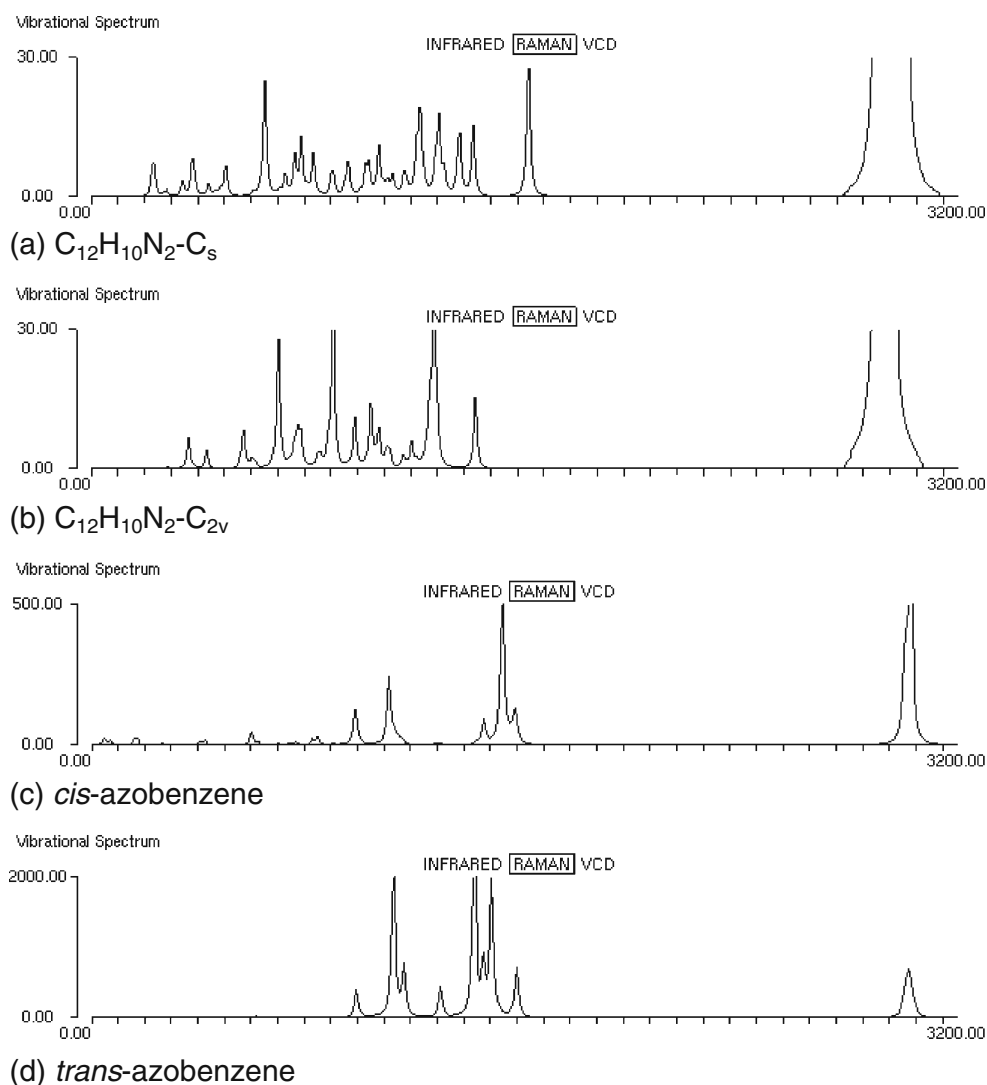
from the parent compounds should be a tremendous aid to detection. However, care needs to be taken as other lower energy stilbene and (presumably) azobenzene isomers, formed theoretically by applying external forces to single pairs of phenyl carbon atoms [1, 2], also have similar such shifts (albeit not so many).

**Table 3** Standard B3LYP/6-31G* SQM scale factors relevant to $C_{14}H_{12}$ and $C_{12}H_{10}N_2$

|  | Type | Scale factor |
|---|---|---|
| Stretch | rCC, rCN, rNN | 0.9207 |
| Stretch | rCH | 0.9164 |
| Bend | ∠CCC, ∠CCN, ∠CNN | 1.0144 |
| Bend | ∠CCH | 0.9431 |
| Torsion | all | 0.9523 |

**Table 4** Predicted B3LYP/6-31G* ^{13}C and ^{1}H NMR chemical shifts (absolute) in the various $C_{14}H_{12}$ isomers reported in this work

|  | *trans*-stilbene | *cis*-stilbene | $C_{14}H_{12}$-$C_s$ | $C_{14}H_{12}$-$C_{2v}$ |
|---|---|---|---|---|
| [13]C Atom |  |  |  |  |
| C1 | 60.0 | 59.0 | 149.9 | 149.3 |
| C2 | 73.5 | 68.6 | 145.4 | 151.9 |
| C3 | 68.0 | 68.8 | 63.6 | 154.8 |
| C4 | 69.2 | 69.3 | 65.0 | 155.6 |
| C5 | 67.8 | 68.0 | 151.4 | 154.8 |
| C6 | 65.2 | 66.1 | 151.3 | 151.9 |
| C7 | 68.1 | 64.7 | 51.2 | 50.0 |
| [1]H Atom[a] |  |  |  |  |
| H2 | 24.6 | 24.6 | 29.3 | 29.3 |
| H3 | 25.0 | 25.2 | 26.0 | 29.1 |
| H4 | 25.1 | 25.2 | 26.2 | 29.4 |
| H5 | 25.0 | 25.0 | 29.2 | 29.1 |
| H6 | 25.2 | 25.2 | 29.4 | 29.3 |
| H7 | 25.4 | 25.9 | 25.6 | 25.5 |

[a] H atoms numbered according to the carbon atom they are attached to

**Table 5** Predicted B3LYP/6-31G* $^{13}$C, $^{15}$N and $^1$H NMR chemical shifts (absolute) in the various $C_{12}H_{10}N_2$ isomers reported in this work

| | *trans*-azo | *cis*-azo | $C_{12}H_{10}N_2$-$C_s$ | $C_{12}H_{10}N_2$-$C_{2v}$ |
|---|---|---|---|---|
| $^{13}$C/$^{15}$N Atom | | | | |
| C1 | 45.0 | 43.3 | 116.3 | 114.2 |
| C2 | 82.0 | 81.5 | 143.9 | 149.0 |
| C3 | 68.0 | 68.9 | 64.8 | 154.0 |
| C4 | 65.1 | 69.6 | 64.6 | 155.6 |
| C5 | 67.6 | 66.9 | 151.6 | 154.0 |
| C6 | 61.6 | 68.6 | 148.1 | 149.0 |
| N7 | -261.9 | -302.3 | -370.6 | -373.9 |
| $^1$H Atom[a] | | | | |
| H2 | 24.3 | 26.2 | 28.9 | 28.9 |
| H3 | 24.9 | 25.3 | 26.0 | 29.0 |
| H4 | 24.9 | 25.2 | 26.1 | 29.3 |
| H5 | 24.7 | 24.7 | 29.1 | 29.0 |
| H6 | 24.2 | 24.6 | 29.0 | 28.9 |

[a] H atoms numbered according to the carbon atom they are attached to

## Conclusions

In this work we have reported on the discovery of two structurally very interesting, new high energy but potentially kinetically stable, symmetrical "fused sandwich" isomers of both *cis*-stilbene and the related *cis*-azobenzene. We have presented simulated IR and Raman vibrational spectra of all four of the new isomers and indicated how they can be distinguished from the parent compounds, *cis*-stilbene and *cis*-azobenzene, by NMR spectroscopy.

Neither of the authors are experimental chemists and so we cannot suggest any practical method to make these compounds, but once again the theoretical approach utilized here, enforced geometry optimization [2, 3], has demonstrated that it is a very useful and powerful tool for discovering potentially new chemical structures.

## References

1. Baker J, Wolinski K, J Comput Chem, in press
2. Wolinski K, Baker J (2009) Mol Phys 107:2403–2417
3. Wolinski K, Baker J (2010) Mol Phys 108:1845–1856
4. Hohenberg P, Kohn W (1964) Phys Rev B 136:864–871
5. Kohn W, Sham L (1965) Phys Rev A 140:1133–1138
6. Becke AD (1993) J Chem Phys 98:5648–5652
7. Hertwig R, Koch W (1997) Chem Phys Lett 268:345–351
8. Ditchfield R, Hehre WJ, Pople JA (1971) J Chem Phys 54:724–728
9. *PQS* version 4.0, beta, Parallel Quantum Solutions, 2013 Green Acres Road, Suite A, Fayetteville, Arkansas 72703, U.S.A. Email: sales@pqs-chem.com; URL: http://www.pqs-chem.com
10. Baker J, Jarzecki AA, Pulay P (1998) J Phys Chem A 102:1412–1424