CHEMCOMM
Communication
www.rsc.org/chemcomm

Thermochromism of overcrowded bistricyclic aromatic enes (BAEs). A theoretical study†

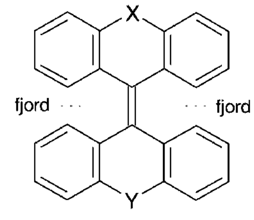
P. Ulrich Biedermann,[ab] John J. Stezowski[c] and Israel Agranat*[a]

[a] *Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem 91904, Israel. E-mail: isria@vms.huji.ac.il; Fax: +972-2-6511907*
[b] *Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany*
[c] *Department of Chemistry, University of Nebraska-Lincoln, Lincoln NE-68588-0304, USA*

Received (in Cambridge, UK) 26th February 2001, Accepted 4th April 2001
First published as an Advance Article on the web 9th May 2001

A criterion for thermochromism has been derived from *ab initio* DFT B3LYP/6-31G* calculations of the *anti*-folded, *syn*-folded and twisted conformations of thermochromic and non-thermochromic overcrowded bistricyclic aromatic enes (BAEs) 1–8: the thermochromic species is the twisted conformation, a necessary condition being a small energy difference, <30 kJ mol^{-1}, between the global minimum *anti*-folded and the thermochromic conformations.

Four score and a dozen years ago the phenomenon of thermochromism—reversible change of color with change of temperature—was revealed in bianthrone (**1**),[1] a leading overcrowded bistricyclic aromatic ene (BAE).[2] The BAEs are attractive substrates for the study of the conformational behavior of overcrowded ethylenes and for the interplay of strain and delocalization effects.[2] Thermochromic and photochromic BAEs and related overcrowded enes serve as candidates for chiroptical molecular switches and molecular motors.[3] Derivatives of **1** are topologically related to hypericin, wide spread in St. Johns Wort, an important remedy for depression.[4]



BAE

	X	Y
1	CO	CO
2	O	O
3	S	S
4	—	—
5	CH=CH	CH=CH
6	—	O
7	—	CO
8	O	CO

The thermochromism of **1** and related BAEs in solution has been attributed to a thermal equilibrium between two distinct and interconvertible conformers ($\mathbf{A} \overset{kT}{\underset{\longleftarrow}{\longrightarrow}} \mathbf{B}$),[5] where **A** is the room temperature, *anti*-folded (**a**), yellow conformer and **B** is the thermochromic, green–blue conformer. It is generally agreed that the thermochromic, piezochromic, and photochromic[6] **B** forms are identical. The prerequisites for thermochromism in BAEs have been a controversial issue.[7] Zwitterionic valence isomers, diradicals, thermally populated triplets, Woodward and Wasserman's electrocyclized isomer, planar, twisted, and double chair conformations have been suggested as the **B** form.[7] Previous studies applying various force fields[6a] and the semiempirical MINDO/3,[8] AM1,[9] and PM3[2c,d] methods failed to rationalize thermochromism in the BAEs series. Although PM3 calculations of the dynamic stereochemistry of BAEs agreed with experiment, they failed to rationalize the thermochromic behavior.[2c,d] We report here a theoretical approach, applying *ab initio* Hartree-Fock (HF) and Density Functional Theory (DFT), with the objective of determining whether a given BAE should be thermochromic.

The homomerous BAEs bianthrone (**1**), dixanthylene (**2**), dithioxanthylene (**3**), bifluorenylidene (**4**), bisdibenzocycloheptenylidene (**5**), and the heteromerous BAEs fluorenylidene-xanthene (**6**), fluorenylidene-anthrone (**7**), and xanthylidene-anthrone (**8**) were subjected to *ab initio* HF/6-31G* and DFT B3LYP/6-31G*[10] calculations using Gaussian 94.[11] All geometries were fully optimized subject to symmetry constraints as indicated. Minima and transition states were verified by computing vibrational frequencies at HF/STO-3G, and B3LYP/STO-3G optimized geometries. The following conformations were calculated: homomerous BAEs **1**–**5**, D_2 twisted (**t**), C_{2h} *anti*-folded (**a**) and C_{2v} *syn*-folded (**s**); **8**, C_2 twisted (**t**), C_s *anti*-folded with uneven degrees of folding (**au**), and C_s *syn*-folded with uneven degrees of folding (**su**); **6** and **7**, C_2 twisted (**t**), C_s *anti*-folded with uneven degrees of folding (**au**). Table 1 gives the calculated B3LYP/6-31G* and HF/6-31G* relative energies (ΔE_{rel}) of the optimized conformations. The experimental enthalpy values of the thermochromic **B** form, $\Delta H_{A \rightarrow B}$, and some geometrical parameters are also included.

According to the B3LYP/6-31G* results, three types of conformational behavior appear:

Table 1 Calculated and experimental relative energies of BAEs[a]

		Twist[b] ω[d]	Fold[b] φ[e]	HF[c] ΔE_{rel}	B3LYP[b] ΔE_{rel}	Exptl. $\Delta H_{A \rightarrow B}$
1	**a**-C_{2h}	0.0	41.5	0.0	0.0	
1	**t**-D_2	55.0	4.4	66.4	12.0	12.6[5f,13]
1	**s**-C_{2v}	0.0	42.5	45.3	43.4	
2	**a**-C_{2h}	0.0	40.9	0.0	0.0	
2	**t**-D_2	49.7	2.7	71.1[f]	24.4	23.4[5c]
2	**s**-C_{2v}	0.0	42.5	41.2	38.1	
3	**a**-C_{2h}	0.0	49.5	0.0	0.0	
3	**s**-C_{2v}	0.0	51.9	38.2	35.0	
3	**t**-D_2	57.8	8.0	159.5[f]	86.6	
4	**t**-D_2	34.0	2.4	0.0	0.0	
4	**a**-C_{2h}	0.0	23.5	33.4	39.0	
4	**s**-C_{2v}	0.0	20.5	73.1[f]	74.3[g]	
5	**a**-C_{2h}	0.0	52.4	0.0	0.0	
5	**s**-C_{2v}	0.0	55.6	20.4	19.9	
5	**t**-D_2	65.9	22.6	268.0[f]	166.9[f]	
6	**t**-C_2	42.2	3.9/3.8	0.0	0.0	
6	**au**-C_s	0.0	47.2/15.1	−22.5	4.5	
7	**t**-C_2	44.1	6.5/4.5	0.0	0.0	
7	**au**-C_s	0.0	47.2/16.4	−24.1	5.5	
8	**au**-C_s	0.0	42.1/40.3	0.0	0.0	
8	**t**-C_2	53.3	2.2/4.2	60.6	10.8	14.6[5c]
8	**su**-C_s	0.0	44.4/40.2	43.0	41.3	

[a] Energies in kJ mol^{-1}; the conformations are minima unless noted otherwise. [b] B3LYP/6-31G*. [c] HF/6-31G*. [d] Pure twist of the central ethylene bond: $\omega = \frac{1}{2}(\tau_{C9a\text{-}C9\text{-}C9'\text{-}C9a'} + \tau_{C8a\text{-}C9\text{-}C9'\text{-}C8a'})$. [e] Folding of the tricyclic moieties defined by the dihedral φ of the least-squares-planes of the aromatic rings. [f] Transition state. [g] Second order saddle point.

---

† Electronic supplementary information available: semiempirical and *ab initio* total energies of BAEs, calculated and experimental relative energies of BAEs, selected B3LYP/6-31G* geometric parameters and frontier orbital energies. See http://www.rsc.org/suppdata/cc/b1/b101797g/

DOI: 10.1039/b101797g

Type 1: BAEs **1**, **2**, and **8** have *anti*-folded global minima **a**. For **1** and **2**, *anti*-folded conformations were found in the X-ray crystal structures, which correspond to the respective **A** forms.[2b,c] The twisted conformations **t** are only $\Delta E_{\text{rel}}(\mathbf{1})$ = 12.0 kJ mol^{-1}, $\Delta E_{\text{rel}}(\mathbf{2})$ = 24.4 kJ mol^{-1}, and $\Delta E_{\text{rel}}(\mathbf{8})$ = 10.8 kJ mol^{-1} higher in energy and thus may be populated thermally. The DFT calculated energies are in very good agreement with the experimentally determined enthalpies of the blue–green thermochromic **B** forms:[12] $\Delta H_{\text{A}\rightarrow\text{B}}(\mathbf{1})$ = 12.6 kJ mol^{-1},[5f,13] $\Delta H_{\text{A}\rightarrow\text{B}}(\mathbf{2})$ = 20.5,[5b] or 23.4[5c] kJ mol^{-1}, and $\Delta H_{\text{A}\rightarrow\text{B}}(\mathbf{8})$ = 14.6 kJ mol^{-1}.[5c] The *syn*-folded conformations of **1**, **2**, and **8** are considerably higher in energy ($\Delta E_{\text{rel}}(\mathbf{s})$ = 38 to 43 kJ mol^{-1}). While the *anti*- and *syn*-folded conformations are colorless or pale yellow, the high twist in the central double bond reduces the π-overlap causing a substantial red shift and smaller HOMO–LUMO gaps in twisted conformations. This rationalizes the color change observed in thermochromic BAEs. Even a small population of the twisted conformation at elevated temperatures leads to a striking change of the visible color from yellow to green or blue-green (Fig. 1).

Type 2: BAEs **3** and **5** also adopt *anti*-folded conformations as global minima. However, in these cases the *syn*-folded conformations **s** are more stable than the twisted conformations **t**. The B3LYP/6-31G* conformational energies are $\Delta E_{\text{rel}}(\mathbf{s})$ = 35.0 and 19.9 kJ mol^{-1}, while $\Delta E_{\text{rel}}(\mathbf{t})$ = 86.6 and 166.9 kJ mol^{-1} for **3** and **5** (in **5**, **t** is a transition state). The twisted conformations cannot be populated in thermal equilibrium, explaining the absence of thermochromism in these compounds.

Type 3: BAEs **4**, **6**, and **7** have twisted global minima. This is in accord with the deep color of the three BAEs (thermochromic **B** form) at room temperature. The *anti*-folded conformation of **4** is considerably higher in energy, $\Delta E_{\text{rel}}(\mathbf{a})$ = 39.0 kJ mol^{-1}, while the folded conformations of **6** and **7** are only $\Delta E_{rel}(\mathbf{au})$ = 4.5 and 5.5 kJ mol^{-1} higher than the twisted conformations. Thus, the folded conformations of **6** and **7** may easily be populated. Packing effects may favor the folded conformations.[14] Indeed, yellow crystals with folded conformations have been observed in **6** and **7**.[2b,14]

The relative B3LYP/6-31G* conformational energies $\Delta E_{\text{rel}}(\mathbf{t})$ agree within ±4 kJ mol^{-1} with the experimental $\Delta H_{\text{A}\rightarrow\text{B}}$ of the thermochromic species. On the other hand, the Hartree-Fock results show substantial, systematic deviations from the experimental data. For HF/6-31G*, the average absolute error is 50 kJ mol^{-1}. The conformational energies of the twisted thermochromic **B** conformers are systematically overestimated by the HF calculations. According to the HF/6-31G* results, **s** is more stable than **t** in **1**, **2**, and **8**, leading to a Type 2 conformational behavior (non-thermochromic). Furthermore, at HF/6-31G*, **6** and **7** would have folded global minima and should be yellow at room temperature.

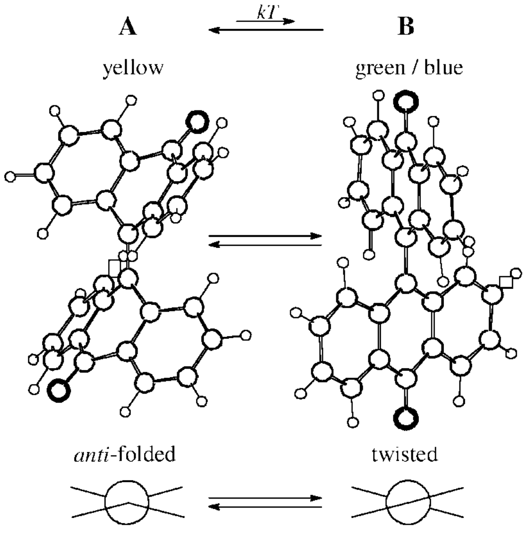


Fig. 1 The mechanism of thermochromism of BAEs using 3D structures of bianthrone (**1**) calculated at B3LYP/6-31G*.

The unique molecular architecture of BAEs gives rise to three conformations, *anti*-folded, *syn*-folded and twisted. Each conformation represents a different compromise between π-delocalization and steric strain. The bridges **X** and **Y** play an important role in the relative stability of the three conformations, leading to thermochromism in favorable cases.

In conclusion, the following necessary conditions for the thermochromic behavior of BAEs are deduced: (i) the global minimum of a thermochromic BAE is *anti*-folded (**a**) or unevenly *anti*-folded (**au**), whereas the thermochromic conformation is twisted (**t**); (ii) the energy difference between these conformations is small: $(E(\mathbf{t}) - E(\mathbf{a})) < 30$ kJ mol^{-1}. While previous theoretical studies and *ab initio* Hartree-Fock calculations are flawed, giving conformational energies of twisted conformations that are systematically too high, inclusion of electron correlation *via* the DFT method solves this difficulty. The B3LYP/6-31G* $\Delta E_{\text{rel}}(\mathbf{t})$ and the experimental $\Delta H_{\text{A}\rightarrow\text{B}}$ of the thermochromic species agree within ±4 kJ mol^{-1}.

Notes and references

1 H. Meyer, *Monatsh. Chem.*, 1909, **30**, 165; H. Meyer, *Ber. Dtsch. Chem. Ges.*, 1909, **42**, 143.

2 (*a*) J. Sandström, *The chemistry of double-bonded functional groups*, Supplement A3, S. Patai, Ed., Wiley, 1997, p. 1253; (*b*) G. Shoham, S. Cohen, M. R. Suissa and I. Agranat, *Molecular Structure: Chemical Reactivity and Biological Activity*, J. J. Stezowski, J.-L. Huang, M.-C. Shao, Eds., IUCr Crystallographic Symposia 2, Oxford University Press, Oxford, 1988, p. 290; (*c*) P. U. Biedermann, J. J. Stezowski and I. Agranat, *Advances in Theoretically Interesting Molecules*, Vol. 4, R. P. Thummel Ed., JAI Press, Stamford, CT, 1998, p 245; (*d*) P. U. Biedermann, J. J. Stezowski and I. Agranat, *Eur. J. Org. Chem.*, 2001, 15.

3 B. L. Feringa, A. M. Schoevaars, W. F. Jager, B. de Lange and N. P. M. Huck, *Enantiomer*, 1996, **1**, 325; N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.*, 2000, **100**, 1789.

4 K. Linde, G. Ramirez, C. D. Mulrow, A. Pauls W. Weidenhammer and D. Melchart, *Brit. Med. J.*, 1996, **313**, 253; M. Philipp, R. Kohnen and K.-O. Hiller, K. Linde and M. Berner, *Brit. Med. J.*, 1999, **319**, 1534.

5 (*a*) W. T. Grubb and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 1950, **72**, 419; (*b*) W. Theilacker, G. Kortüm and G. Friedheim, *Ber. Dtsch. Chem. Ges.*, 1950, **83**, 508; (*c*) Y. Hirschberg and E. Fischer, *J. Chem. Soc.*, 1953, 629; (*d*) G. Kortüm, *Angew. Chem.*, 1958, **70**, 14; (*e*) Z. R. Grabowski and M. S. Balasiewicz, *Trans. Faraday Soc.*, 1968, **64**, 3346; (*f*) Y. Tapuhi, O. Kalisky and I. Agranat, *J. Org. Chem.*, 1979, **44**, 1949.

6 E. Fischer, *Rev. Chem. Intermed.*, 1984, **5**, 393; K. A. Muszkat, *The chemistry of quinonoid compounds*, Vol. 2, S. Patai, Z. Rappoport, Eds., Wiley, 1988, p. 203; W. H. Laarhoven, in: *Photochromism, Molecules and Systems*, H. Dürr and H. Bouas-Laurent Eds., Elsevier, Amsterdam, 1990, p. 970.

7 J. H. Day, *Chem. Rev.*,1963, **63**, 65; G. Kortüm, *Ber. Bunsen-Ges. Phys. Chem*, 1974, **78**, 391; R. B. Woodward and E. Wasserman, *J. Am. Chem. Soc.*, 1959, **81**, 5007.

8 O. Kikuchi and Y. Kawakami, *J. Mol. Struct. (Theochem)*, 1986, **137**, 365.

9 P. Sommer-Larsen, T. Bjørnholm, M. Jørgensen, K. Lerstrup, P. Frederiksen, K. Schaumburg, K. Brunfeldt, K. Bechgaard, S. Roth, J. Poplawski, H. Byrne, J. Anders, L. Eriksson, R. Wilbrandt and J. Frederiksen, *Mol. Cryst. Liq. Cryst.*, 1993, **234**, 89.

10 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200.

11 Gaussian 94, Revision E.2, M. J. Frisch, J. A. Pople *et al.*, Gaussian, Inc., Pittsburgh PA, 1995.

12 The contributions of the zero-point corrections and thermal corrections to enthalpy to the relative conformational energies (conversion of ΔE_{rel} to ΔH) are insignificant (less than ±2 kJ mol^{-1} at B3LYP/STO-3G) and therefore neglected.

13 Earlier experimental values for $\Delta H_{\text{A}\rightarrow\text{B}}(\mathbf{1})$ are: 11.3,[5e] 13.0,[5a] 13.8,[5a] 16.3,[5a] 14.2,[5b] 14.2,[5d] and 14.6 kJ mol^{-1}.[5c] $\Delta E_{\text{rel}}^{\text{B3LYP/6-31G*}}$ agrees best with the more recent lower experimental values.[5e,5f]

14 A. Levy, P. U. Biedermann and I. Agranat, *Org. Lett.*, 2000, **2**, 1811.