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Overcrowded Enes of the Tricycloindane-1,3-dione Series: Interplay of Twisting, Folding and Pyramidalization

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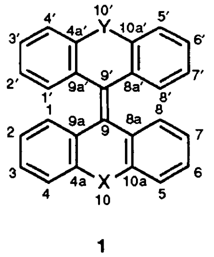
MNDO-PM3 calculations have revealed three low energy conformations for the overcrowded ene 2-(thioxanthen-9-ylidene)indane-1,3-dione **2**, two of which, a *syn*-pyramidalized C_s conformer (yellow solvated crystals) and a C_1 folded-twisted conformer (orange unsolvated crystals), were characterized by single crystal X-ray diffraction techniques, and a C_2 twisted, non-pyramidalized conformer, which may be present in the thermochromic deep-red crystals obtainable by sublimation at $T > 140$ °C.

Overcrowded enes deviate from coplanarity by two principal modes: twisting around the double bond and bending (hence pyramidalization of the ene carbon atoms).[1–3] Bistricyclic aromatic enes **1**[4] have previously served as attractive substrates for the study of the stereochemistry of overcrowded enes.[4,5] Molecules **1** with central six-membered rings are mostly folded while **1** with central five-membered rings are mostly twisted. Both types may be pyramidalized.[4,6–8] Thermochromism and photochromism were observed for bianthrone (**1**, X, Y = C=O) and dixanthenylidene (**1**, X, Y = O), but not in bifluorenylidene (**1**, X, Y = –).[9,10] These phenomena have been attributed to twisted thermochromic (and photochromic) conformations generated from ground-state folded conformations. An attempt to characterize the molecular structure of the thermochromic species of dixanthenylidene crystallographically was apparently unsuccessful.[11] We report here on the interplay of twisting, folding and pyramidalization within two distinct, stable, interconvertable conformations of a single overcrowded aromatic ene, 2-(thioxanthen-9-ylidene)indane-1,3-dione **2**.[12] We note a high degree of *syn*-pyramidalization[6c] in both a folded, non-twisted conformation with C_s symmetry (yellow crystals, $\mathbf{2}_y$) and a chiral (racemic), folded-twisted conformation with C_1 symmetry (orange crystals, $\mathbf{2}_o$) of **2**. Thermochromism was observed at elevated temperatures for crystals of **2** (deep-red crystals, $\mathbf{2}_r$).

Reversible conversion of crystals $\mathbf{2}_o$ to $\mathbf{2}_r$ can be carried out repeatedly without visible degradation. Differential scanning calorimetry (DSC) experiments starting with $\mathbf{2}_o$ indicate that the sample converts to $\mathbf{2}_r$ without undergoing a detectable phase change. The first observable endotherm in the DSC curve corresponds to melting (234–235 °C); upon cooling to room temperature at 0.1° min^{-1}, an exotherm is observed at 213 °C. When cooled more rapidly, no exotherm was seen in the DSC curve and the resultant sample ($\mathbf{2}_{g1}$) displayed a glass-like appearance. Upon reheating, samples of $\mathbf{2}_{g1}$ pass through an exothermic phase transition at 120–123 °C, to give a new phase $\mathbf{2}_{g2}$, which is also glass-like in appearance. Glasses $\mathbf{2}_{g1}$ and $\mathbf{2}_{g2}$ were both dark red. Powder diffraction patterns measured from the glasses $\mathbf{2}_{g1}$ and $\mathbf{2}_{g2}$ indicated that, although some change had taken place both samples were amorphous. Solid-state ESR (electron spin resonance) experiments carried out at room temperature on samples of glass $\mathbf{2}_{g1}$ and $\mathbf{2}_{g2}$ reveal the presence of radicals, most likely at low concentrations. In contrast, crystalline samples of $\mathbf{2}_o$ do not give ESR signals. The ESR signal disappeared when a sample was sublimed in an ESR tube and remeasured.

Semi-empirical calculations (MNDO-PM3 parameterization) suggest a purely twisted conformation, $\mathbf{2}_t$, with C_2 symmetry as a local minimum in the conformational space of **2**. In contrast to **2**, the related overcrowded 2-(xanthen-9-ylidene)indane-1,3-dione,[13] **3** (dark-bronze–red crystals, $\mathbf{3}_{rb}$) displays a highly twisted, non-folded, conformation with C_2 symmetry (symmetry axis along the ethylenic bond), devoid of pyramidalization. The two fjord regions in **2** and **3** are characterized by a common overcrowded ene and close intramolecular contacts between the carbonyl oxygen atoms and the aromatic rings (*e.g.* $C_{1'}\cdots O_1$ and $H_{1'}\cdots O_1$).

The two pseudopolymorphic crystalline forms of **2** were grown by different techniques: the yellow crystals from a toluene solution into which some acetic acid was incorporated by vapour transport and the orange crystals by sublimation *in vacuo* at elevated temperature [185 °C and *ca.* 0.01 Torr (1 Torr = 133.322 Pa)]. The dark-red crystals were observed in the sublimation tube at the entrance to the furnace; they converted to the orange form on cooling. Crystals could be



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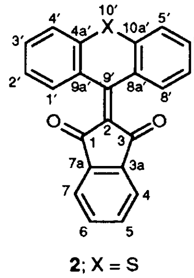

2; X = S
3; X = O

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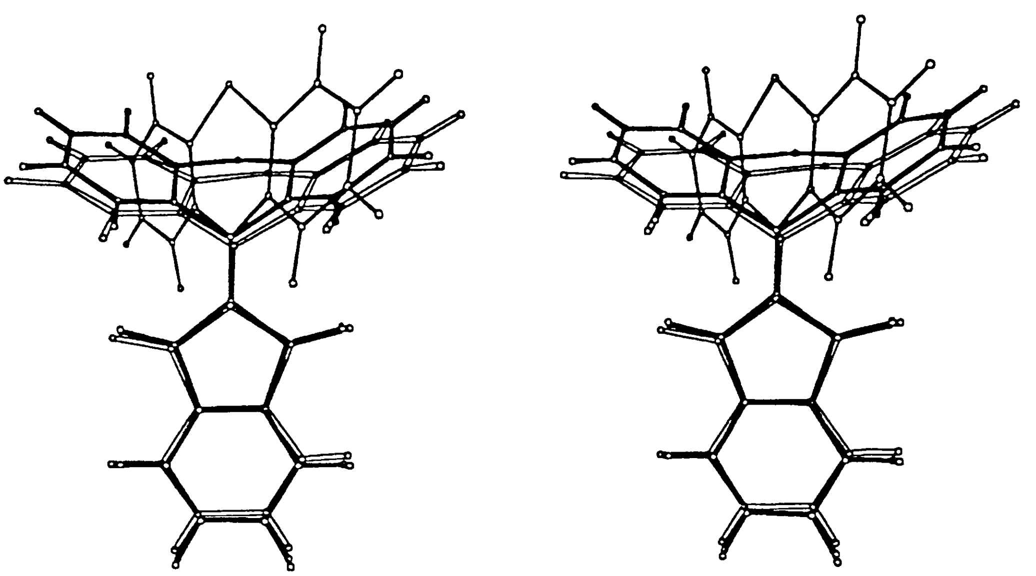

Fig. 1 Stereoscopic superposition of crystal structure results for $\mathbf{2}_{\mathrm{y}}$ (thick filled bonds) and $\mathbf{2}_{\mathrm{o}}$ (open bonds) and the calculated conformation for $\mathbf{2}_{\mathrm{t}}$ (thin filled bonds)

Table 1 Conformational parameters of calculated structures ($\mathbf{2}_{\mathrm{f}}$, $\mathbf{2}_{\mathrm{ft}}$, $\mathbf{2}_{\mathrm{t}}$, $\mathbf{3}_{\mathrm{f}}$, $\mathbf{3}_{\mathrm{ft}}$ and $\mathbf{3}_{\mathrm{t}}$) and crystal structures ($\mathbf{2}_{\mathrm{y}}$, $\mathbf{2}_{\mathrm{o}}$ and $\mathbf{3}_{\mathrm{rb}}$)

	$\mathbf{2}_{\mathrm{f}}$	$\mathbf{2}_{\mathrm{ft}}$[b]	$\mathbf{2}_{\mathrm{t}}$	$\mathbf{3}_{\mathrm{f}}$	$\mathbf{3}_{\mathrm{ft}}$[b]	$\mathbf{3}_{\mathrm{t}}$	$\mathbf{2}_{\mathrm{y}}$[c]	$\mathbf{2}_{\mathrm{o}}$[b]	$\mathbf{3}_{\mathrm{rb}}$
Fold[a]	49.5	45.0	—	40.8	35.6	—	53.5(1)	44.1(2)	—
Twist	0.0	14.0	45.5	0.0	17.3	42.5	0.0(0)	11.1(4)	41.5
C(2)=C(9′)/pm	135.0	135.4	138.0	135.2	135.8	137.4	136.1((3)	136.6(4)	140.6
C(4a′)–X(10′)/pm	176.6	175.9/176.3	173.8	138.9	138.4/138.7	137.4	176.1(2)	175.7/175.1(3)	136.4
C(4a′)–X(10′)–C(10a′)/°	98.4	98.8	102.9	112.4	113.1	117.0	98.3(1)	99.6(2)	119.4
C(9a′)–C(4a′)–X(10′)/°	121.3	121.3/122.6	124.9	121.7	121.6/122.6	124.0	120.6(1)	121.0/122.2(2)	122.3
C(9′)–C(9a′)–C(4a′)/°	118.0	120.2/118.7	123.3	116.6	118.2/117.0	120.2	118.4(1)	120.0/118.3(2)	120.2
C(8a′)–C(9′)–C(9a′)/°	111.6	113.1	120.1	109.4	110.5	114.7	112.7(1)	114.0(2)	115.6
C(4a′)···C(10a′)/pm	267.5	267.4	271.7	230.8	231.2	234.2	266.1(2)	267.0(5)	235.6
O(1)···C(1)/pm	286.1	284.9/266.9	295.5	284.0	279.9/270.6	296.7	283.8(2)	279.6/280.5(4)	293.0
O(1)···H(1)/pm	272.0	273.7/188.7	254.6	255.6	257.6/182.7	244.1	264.2(19)	276.0/230.6(30)	233.4

[a] Fold: defined by the dihedral angles of the least-square planes of benzene rings in tricyclic unit. [b] Chemically but not crystallographically equivalent values are indicated by the symbol (/). [c] Average value for the two crystallographically independent molecules.

cycled repeatedly between the room temperature form (orange crystals) and the thermochromic form (deep-red crystals) for several cycles without visible degradation. Not unexpectedly, UV–VIS (absorption at 332 nm, ε = 14000 and at 440 nm ε = 8400) and ^{1}H NMR spectra [400 MHz, $CDCl_3$, δ 8.07–8.02 (m, $H_{1'}$, $H_{8'}$), 7.91–7.86 (m, H_4, H_7), 7.78–7.74 (m, H_5, H_6), 7.68–7.64 (m, $H_{4'}$, $H_{5'}$) and 7.45–7.40 (m, $H_{2'}$, $H_{3'}$, $H_{6'}$, $H_{7'}$)] measured for solutions prepared from either pseudopolymorph were the same. Crystallographic data and model refinement characterization follow. Yellow form, $\mathbf{2}_{\mathrm{y}}$: space group *Pbam* with a = 1059.7(1), b = 2037.3(4), c = 1651.1(3) pm; formula per asymmetric unit $C_{22}H_{12}O_2S\cdot\frac{1}{2}C_2H_4O_2$; (acetic acid solvate) intensity data were collected using a Siemens P3F diffractometer to $2\theta_{\max}$ = 70° with monochromatized Mo-Kα radiation using an ω-scan technique; the refinement converged with R = 0.048 with 6502 data contributing to the refinement of 318 variables. Orange form, $\mathbf{2}_{\mathrm{o}}$: space group $P2_1/n$ with a = 952.7(2), b = 803.7(2), c = 2135.2(4) pm and β = 94.14(1)°; formula per asymmetric unit $C_{22}H_{12}O_2S$. Intensity data were collected as described above to a $2\theta_{\max}$ = 55°. However, the data set was truncated to $2\theta_{\max}$ = 50° for refinement owing to lack of significant data at higher angles; refinement converged at R = 0.051 for 2450 reflections contributing to the refinement of 274 variables. Both crystal structure models were refined with anisotropic displacement parameters for non-hydrogen atoms and isotropic displacement parameters for hydrogen atoms. More details of the refinements will be published at a later date.[†]

Both molecules in $\mathbf{2}_{\mathrm{y}}$ have a purely folded C_s conformation (average folding angle 53.5°) with *syn*-pyramidalization: substantial for atom C_2 (average χ = 13°)[4,6a] and small for atom $C_{9'}$ (average χ = 3°). The acetic acid solvate molecules are hydrogen-bonded dimers *via* their carboxylate groups. The dimers are intercalated between molecules of $\mathbf{2}_{\mathrm{y}}$ and do not appear to influence the conformations of the latter. $\mathbf{2}_{\mathrm{o}}$ has a composite folded-twisted C_1 conformation. Its folding angle (44.1°) is smaller than those in $\mathbf{2}_{\mathrm{y}}$; it has a substantial ethylenic twist (11°) and somewhat higher *syn*-pyramidalization (C_2: χ = 15°, C_9: χ = 3°). A stereoscopic superposition diagram illustrating the conformations of $\mathbf{2}_{\mathrm{y}}$ and $\mathbf{2}_{\mathrm{o}}$ is displayed in Fig. 1. Selected structural parameters pertaining to the conformations of **2** and **3** are given in Table 1; $\mathbf{3}_{\mathrm{rb}}$ has a twisted C_2 conformation (ethylenic twist 41.5°).[13] Its C_2 axis (through atoms C_2, $C_{9'}$ and $O_{10'}$) prohibits folding and pyramidalization. In contrast to $\mathbf{2}_{\mathrm{y}}$ and $\mathbf{2}_{\mathrm{o}}$, the tricyclic moiety of $\mathbf{3}_{\mathrm{rb}}$ is

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[†] Atomic coordinates, bond lengths and angles, and atomic displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

nearly planar. The molecular conformation in the thermochromic red crystals, $\mathbf{2}_r$ is tentatively assigned to be twisted, such as $\mathbf{2}_t$.

MNDO-PM3[14] calculations indicate that all three conformations are *bona fide* energy minima in the conformational space of **2** and **3**. The folded-twisted conformation ($\mathbf{2}_{ft}$) and the twisted form ($\mathbf{2}_t$) were higher in energy than $\mathbf{2}_f$ by 1.9 and 12.3 kcal mol^{-1} (1 cal = 4.184 J), respectively. Conformation $\mathbf{3}_{ft}$ is very slightly lower in energy ($\Delta E = -0.1$ kcal mol^{-1}) than the $\mathbf{3}_f$; conformation $\mathbf{3}_t$ is considerably higher in energy than $\mathbf{3}_f$ ($\Delta E = 5.2$ kcal mol^{-1}).

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