

# Configurational and Conformational Mobility in a Cross-Conjugated Derivative of 1,3-Diketo-2-iminopropane

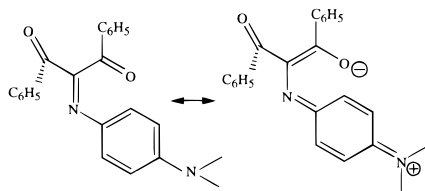
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## ABSTRACT



Mobility of configuration and conformation in the “push–pull” cross-conjugated derivative 1,3-diphenyl-2-(*p*-dimethylaminophenyl)iminopropane-1,3-dione has been investigated by NMR. The energetics of the thermal process that interconnects the *syn*- and *anti*-configurations of the imino group with the atropisomeric conformations of the skewed benzoyl groups are defined. It is proposed that a symmetric Y-delocalized transition state thermally interconnects the inversion of the imino configurations with the mobile interchange of the skewed benzoyl conformations. This connection is observable through a unique NMR window.

The concepts of cross-conjugation<sup>1</sup> and Y-delocalization<sup>2</sup> have been part of the lexicon of chemistry for a number of years.<sup>3</sup> Whether the underlying  $\sigma$ -Y-shaped atomic frameworks are capable of supporting fully conjugated  $\pi$ -electron delocalized and stabilized systems has generated considerable debate.<sup>4</sup> Recently we have shown that unconstrained  $\sigma$ -Y-frameworks, supporting cross-conjugated  $\pi$ -systems, have a skewed geometry.<sup>5</sup> In this Letter we report additional examples of unconstrained, cross-conjugated systems that are capable of sampling Y-delocalization. Instead of  $\pi$ -delocalized planarity, the most obvious conformational hallmark in our systems is mobility that equilibrates energetically separable configurations.

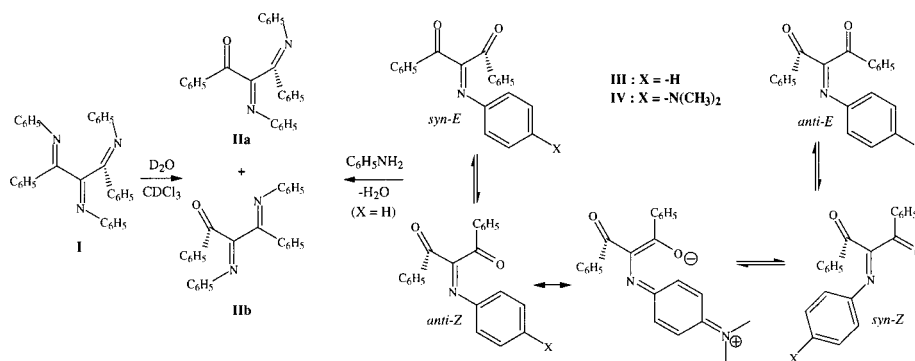
Serendipity entered into our investigations when we noted that the <sup>15</sup>N-labeled NMR sample of the tris(phenylimino)-

1,3-diphenyl-1,2,3-propanetrione, **I**, that we laboriously prepared in low yield,<sup>6</sup> had begun to slowly decompose hydrolytically when stored in “ultrapure” CDCl<sub>3</sub> in a freezer for several months. (The “ultrapure” solvent apparently contained adventitious heavy water.) Examination of this mixture by <sup>1</sup>H-decoupled <sup>15</sup>N NMR, after equilibrium was reached, indicated that additional resonance bands had appeared in relative amounts of 12% and 4% with respect to the starting triimine resonance bands. The 12% resonances appeared at  $\delta = 333.6$  and 359.1 ppm (vs <sup>15</sup>NH<sub>3</sub>) as singlets while the 4% resonances appeared at  $\delta = 350.3$  and 355.6 ppm as doublets having <sup>3</sup>J<sub>N–N</sub> = 2.7 Hz.<sup>5</sup> We attributed the 12% resonances to hydrolytically derived **IIa** while the 4% resonance doublets were attributed to **IIb** (see Scheme 1) and we surmised that these 1-keto-2,3-diiminopropane derivatives were an equilibrating 3:1 mixture of atropisomers. We assumed further that the conformational and configurational structures shown in Scheme 1 for **IIa** and **IIb** were most reasonable on the basis of our previous experience with

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(4) (a) Wiberg, K. *J. Am. Chem. Soc.* **1990**, *112*, 4177–4182. (b) Shancke, A. *J. Phys. Chem.* **1994**, *98*, 5234–5239. (c) Traetteberg, M.; Hopf, H. *Acta Chem. Scand.* **1994**, *48*, 989–993.  
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Scheme 1



these types of cross-conjugated systems.<sup>6</sup> Further investigations as to the equilibrating nature of these atropisomers were precluded, however, by the scarce availability of  $^{15}N$ -labeled **II**. Consequently we examined a more easily prepared derivative, unlabeled **III**. (The  $^{13}C$  and  $^1H$  NMR spectra of pure, unlabeled **II** were complex but it was apparent that a mixture of at least two isomers was present.)

The 1,3-diketo-2-iminopropane derivative, **III**, can have four distinct atropisomeric forms. The phenylimino group can either be *syn* or *anti* to the conformationally skewed benzoyl group or the planar conjugated portion of the molecule can occupy an *s-cis* (*Z*) or *s-trans* (*E*) configuration (Scheme 1). Interconversion of the four atropisomers is easily envisioned by rotating the benzoyl groups into and out of the plane of the imino group. Our derived NMR spectral assignments for **III** are displayed in Table 1 and are consistent with **III** being a rapidly equilibrating mixture of these four possible atropisomers, where *anti-Z-III* and *syn-E-III*<sup>7</sup> are the major isomers present. We can implicate the *syn-E-III* structure as being more important than the *syn-Z-III* structure since our previous observations,<sup>6,7</sup> with several model compounds, show that an *s-trans*-configuration for conjugation is preferred in order to avoid lone pair repulsions. The *anti-Z-III* and *syn-Z-III* configurations are implicated as being part of the equilibrium based upon the observation that the crystal structure of the parent **III**, 1,3-diphenyl-1,2,3-propanetrione, exhibits a skewed conformation that is between and closely aligned to these configurations.<sup>8</sup> Unfortunately, we were unable to directly observe the proposed equilibrium involving *anti-Z-III* with *syn-Z-III* or *syn-E-III*. Consequently we turned our attention to the preparation of 1,3-diphenyl-2-(*p*-dimethylaminophenyl)iminopropane-1,3-dione, an example of a “push–pull” system that has proven to be of value in similarly related cross-conjugated derivatives,<sup>9</sup> and investigation of its properties.

Compound **IV** was prepared in the usual manner<sup>5</sup> using *p*-nitroso-*N,N*-dimethylaniline and dibenzoylmethane as the

starting materials. The NMR spectral characteristics of **IV** were analogous to those of **III**<sup>7</sup> and are shown in Table 1.

**Table 1.**  $^1H$  and  $^{13}C$  NMR<sup>a</sup> Chemical Shift Information for Compounds **III** and **IV**

atom no.	<b>III</b> (X = H)		<b>IV</b> (X = N(CH <sub>3</sub> ) <sub>2</sub> )	
	$^1H$ $\delta$ (ppm)	$^{13}C$ $\delta$ (ppm) <sup>a</sup>	$^1H$ $\delta$ (ppm)	$^{13}C$ $\delta$ (ppm)
1	7.51	134.7	7.52	134.4 <sup>b</sup>
2	7.38	129.0	7.37	129.3
3	7.78	129.5	7.73	129.0
4		134.2		134.8
5		196.2		190.3
6		163.8		140.0
7		191.4		189.0
8		135.0		136.1
9	8.30	131.2	7.94	128.7
10	7.55	128.7	7.52	129.5
11	7.68	134.5	7.65	134.4 <sup>b</sup>
12		147.2		135.1
13	7.01	120.7	7.39	125.8
14	7.22	129.2	6.50 <sup>c</sup>	110.9
15	7.07	126.8		152.9
16			3.00	40.6

<sup>a</sup> Assignments were established using appropriate 1D and 2D NMR methods. <sup>b</sup> Separate resonances only at  $-80$  °C. <sup>c</sup> Assignment of H14 based upon an NOE to the  $-N(CH_3)_2$  group of **IV**.

The similarities between **III** and **IV** are apparent, but the differences proved most informative. (1) The carbonyl-C5 shifted upfield by 5.9 ppm and the carbonyl-C7 shifted upfield by 2.4 ppm. The upfield shift of C5 implicates a more highly conjugated *s-trans* system while the shift of C7 implies that the skewed benzoyl group is in a *syn* relationship to a more charged ring than that found in **III**. These

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observations are consistent with the *syn-E-IV* structure being dominant. (2) Comparing position 13 between **III** and **IV**, we note that the proton H13 of **IV** is shifted downfield by 0.38 ppm while the attendant carbon C13 is shifted downfield by 5.1 ppm. The chemical shift changes associated with position 13 can best be accommodated by an *anti* structure, which must also be present as an equilibrium component. Comparing the resonance structures of **IV** seems to corroborate this conclusion (see below). (3) The imine C6 in **IV** is shifted upfield by 23.8 ppm, in comparison to the same position in **III**, which implies that there is considerable negative charge associated with this position. (The position 6 of **IV** is observed as a singlet in the  $^1\text{H}$ -coupled  $^{13}\text{C}$  NMR spectrum.) The large shift upfield at this position in **IV** implicates considerable resonance delocalization of charge as shown in Scheme 1. (4) The *ipso* C15 in **IV** is shifted downfield by 26.1 ppm in comparison to **III** while the *ipso* C12 is shifted upfield by 12.1 ppm. (The former resonance appears as a complex multiplet in the  $^1\text{H}$ -coupled  $^{13}\text{C}$  NMR spectrum while the latter resonance appears as a triplet of triplets having  $^2J_{\text{C-H}} = 8.5$  Hz and  $^3J_{\text{C-H}} = 3.5$  Hz.) These large changes in chemical shift imply that there is considerable charge separation flowing from the push of the dimethylamino group to the pull of the cross-conjugated benzoyl groups as represented by the resonance structure shown in Scheme 1 for **IV**.

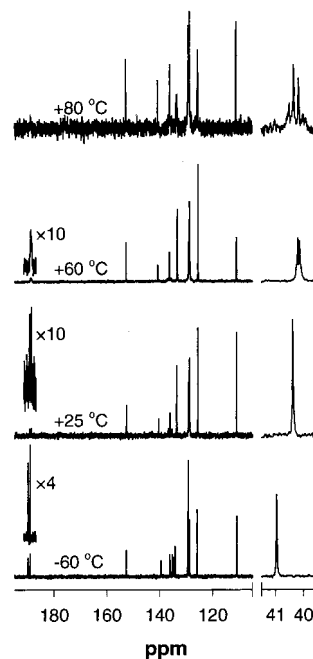
Our structural conclusions were supported by AM1 calculations.<sup>10</sup> The *syn-E-IV* structure was found to be slightly lower in energy than either the *syn-Z-IV* or *anti-Z-IV* structures. Because of a ring–ring interaction, the *anti-E-IV* structure was of much higher energy.

The above comparisons were informative, but in order to make more accurate assessments we had to lower the NMR probe temperature when examining **IV** because it exhibited signs of coalescence signals near room temperature. Consequently, we embarked upon an investigation of the temperature-dependent dynamics displayed by **IV**.

For probing the variable temperature NMR effects displayed by **IV** we investigated the temperature range from  $-90$  to  $+90$  °C in  $10^\circ$  steps ( $\text{CD}_2\text{Cl}_2$  for  $-90$  to  $0$  °C,  $\text{CDCl}_3$  for  $-30$  to  $+60$  °C, and  $\text{Cl}_2\text{CDCDCl}_2$  for  $0$  to  $+90$  °C). Between  $-90$  and  $-10$  °C the 1-D  $^1\text{H}$  and  $^{13}\text{C}$  spectra were observed to be well defined and all resonances were easily identified (Table 1). The spectral resonances began to broaden at  $\sim 0$  °C and subsequently coalesced at  $\sim 60$  °C. At coalescence (between 60 and 65 °C, depending upon the solvent) the proton resonances associated with the dibenzoylmethano portion of the molecule appeared as two broad manifolds centered at  $\delta = 7.5$  and 7.8 ppm while the *N,N*-dimethylanilino portion of the molecule appeared as sharp signals that showed no apparent temperature-dependent chemical shift changes. At  $+90$  °C the protons of rings 1 and 2 appeared as three manifolds centered at  $\delta = 7.4$  ppm (4H), 7.6 ppm (2H), and 7.9 ppm (4H). The carbon spectrum

at coalescence displayed 10 resonances rather than the 16 observed at lower temperatures. The most notable changes were associated with the carbonyl carbons C5 and C7, a broad resonance centered at 189.5 ppm, and the *ipso* carbons C4 and C8, a broad resonance centered at 135.5 ppm. Additionally, resonances for C2, C3, C9, and C10 collapsed to two closely spaced signals at  $\sim 129$  ppm while the resonances for C1 and C11 remained as a single peak at 134.4 ppm. The carbon resonances of ring 3 were unchanged at coalescence in this experiment. Standard manipulation of the variable temperature NMR data<sup>11</sup> according to the Arrhenius equation led to the following thermodynamic parameters near and at coalescence:  $\Delta G^\ddagger = +67$  kJ/mol;  $\Delta H^\ddagger = +63$  kJ/mol;  $\Delta S^\ddagger = -12$  J/mol·K. These derived thermodynamic parameters are consistent with an inversion of configuration mechanism<sup>12</sup> about an imine nitrogen and thus *syn-IV* and *anti-IV* are interconverting at  $\sim +60$  °C.

Closer inspection of the variable temperature CMR experiment between 50 and 70 °C, in  $2^\circ$  steps, revealed the startling observation that the carbon atoms of ring 3, e.g., those off the symmetry axis only, separated into distinguishable topomeric resonances (see Figure 1). The  $^1\text{H}$ -decoupled



**Figure 1.** 1D- $^{13}\text{C}$  NMR spectrum for **IV**. The spectra were taken on a JEOL Eclipse at 100 MHz. The solvent for the  $-60$  °C spectrum was  $\text{CDCl}_2$ , for the 25 and 60 °C spectra the solvent was  $\text{CDCl}_3$ , and the solvent for the 80 °C spectrum was  $\text{CDCl}_2\text{CDCl}_2$ .

carbon resonances for positions 13 and 14 each separated into two closely spaced lines, each having a separation of

(10) The calculated heats of formation were *syn-E-IV*, 350.3 kJ/mol; *syn-Z-IV*, 354.6 kJ/mol; *anti-Z-IV*, 369.9 kJ/mol; *anti-E-IV*, 1402.5 kJ/mol. PC Spartan Plus v1.5, Wavefunction, Inc., 18401 Von Karman Ave., Ste 370, Irvine, CA 92612.

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~0.06 ppm at coalescence. The methyl carbons at position 16 separated into a quartet-like manifold having unequal spacings all near 0.1 ppm at coalescence. To eliminate the possibility that the observed separations were a coupling phenomenon, we examined the off-resonance  $^1\text{H}$ -coupled  $^{13}\text{C}$  NMR of **IV** at +57 °C. Positions C13 and C14 were now a doublet of doublets ( $^1J_{\text{C-H}}(\#13) = 159$  Hz;  $^1J_{\text{C-H}}(\#14) = 162$  Hz) while the methyl groups at position 16 appeared as four quartets having an integrated intensity ratio of ~1:1.6:1.6:1 and  $^1J_{\text{C-H}} = 136$  Hz. More detailed inspection of the separation of the  $^1\text{H}$ -decoupled carbon resonances at positions 13, 14, and 16 revealed that the separations for all three were temperature dependent, increasing from 0 ppm at +45 °C to as much as 0.13 ppm at +70 °C for position 16. We also noticed two other features of importance in this experiment. (1) The separation of the “doublets” for C13 and C14 were equivalent, increasing with temperature to a value of ~0.10 ppm at +70 °C. (2) The separation within the quartet-like resonances associated with position 16 were unequal: the more intense central resonances had a larger separation (0.131 ppm at +70 °C) at all temperatures relative to their separation from the wing resonances (downfield pair, 0.123 ppm; upfield pair 0.115 ppm at 70 °C). The observation of these separations eliminated the possibility of some sort of coupling phenomenon.<sup>13</sup> Consequently, we associate the separate topomeric resonances with an equilibrating mixture of atropisomers, *anti-Z-IV*, *syn-Z-IV*, and *syn-E-IV*, viewed

through the window of an interconversion of conformational and configurational isomers. The relative concentrations of the four atropisomers at any given temperature are unknown at present.

The hallmark of the cross-conjugated systems we have studied is mobility of conformation and configuration. Until we had prepared compound **IV**, however, we were unable to directly observe the proposed structural isomers or skewed conformers we believed were present in these equilibrium systems. Now, through a unique nuclear magnetic resonance window we are able to witness the individual configurational and conformational isomers. Consequently, we can state with some confidence that a Y-delocalized transition state must connect the cross-conjugated atropisomer *anti-Z-IV* with the *syn-E-IV* and *syn-Z-IV* conformers via an activation barrier of about 65 kJ/mol. Experiments to further clarify the thermodynamic parameters associated with this type of fluxional atropisomerism are underway.

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