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A study of the spiropyran-merocyanine system using ion mobility-mass spectrometry: experimental support for the cisoid conformation[†]

Robert A. Rogers, Allison R. Rodier, Jake A. Stanley, Nick A. Douglas, Xiaopeng Li* and William J. Brittain*

The spiropyran-merocyanine system was studied using ion mobility-mass spectrometry (IM-MS) and three major conformers were identified. Assignment of conformers is based on DFT-B3LYP energy minimized structures and collision cross-sections as light-induced changes in IM-MS. The three conformers were assigned to the spiropyran, cisoid and transoid structures.

The photoinduced and thermal isomerization of spiropyrans (SP) have been extensively studied.¹ The first step in the photochemical process is C_{spiro} -O bond cleavage to generate an excited triplet or singlet state that decays within picoseconds and produces a mixture of geometric isomers of merocyanine (MC) that differ in *cis/trans* (*C* or *T*) conformations about the α , β and γ bonds linking the indole and chromene subunits (Scheme 1). For 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline] (6-nitro-BIPS, SP-1), the photochemical reaction proceeds *via* a triplet mechanism followed by intersystem crossing to ³CCC merocyanine and subsequent conversion to ³CTC and ³TTC. Theoretical investigations suggest ³CCC* decays in picoseconds while the lifetime of the ³CTC and ³TTC species is milliseconds.² Evidence for the CTC form of 6-nitro-BIPS comes from laser-desorption/ electron diffraction and excited state dynamics.³



Scheme 1 General structures of SPs **1–3** and their corresponding MCs.

For a thermally equilibrated system, there are eight possible geometric isomers of MC. Studies have demonstrated both zwitterionic⁴ and quinoidal⁵ character for the MC structure. Isomers with the *trans* configuration about the β bond (TTT, TTC, CTT, and CTC) are strongly favoured based on quantum chemical calculations,⁶ time-resolved emission spectroscopy⁷ and NMR.^{7,8} NMR studies based on systems that stabilize the MC isomer through additional aromatic substituents^{8c-e} indicate that TTT (major isomer) and TTC are the predominate isomeric forms in solution.^{7,8d,f} However, these not-commonly studied systems may not reflect the parent system behaviour.^{8c-e} Quantum chemical calculations have shown that TTC is the most stable and TTT second most stable.^{6,8d,f,9} Several computational studies used a reduced atom set to facilitate computations making comparison to the parent system more difficult.

Here we used electrospray ionization (ESI) ion mobility-mass spectrometry (IM-MS)¹⁰ to examine both equilibrated and irradiated samples of spiropyrans **1–3** in methanol (Scheme 1) to gain further experimental insight into the photoisomerization.

IM-MS provides information on the molecules' shapes and sizes based on collision cross-section (CCS), in addition to mass and compositional information. Our interpretation of the IM-MS experimental data argues for presence of a long-lived (>milliseconds) CCX (refers to two of the four MC isomers with *cis* configuration at the central bond) isomer of MC. The lifetime of this proposed species is considerably longer than the sub-nanosecond lifetimes reported previously.³

SP-1 is commercially available and SP-2 and SP-3 were prepared according to literature.¹¹ Each sample was measured under three conditions: (1) dark equilibration for ~24 hours, (2) UV irradiation (300–400 nm), and (3) visible irradiation (>400 nm). The irradiation was performed *ex situ* for two minutes per fresh sample in a quartz cuvette and then transferred and injected *via* syringe immediately (<1 min) after treatment. SP degradation was minimized by using fresh samples from equilibrated stock solutions of each compound.

Buncel and co-workers¹² reported that acid catalysis of SP-1 produces the O-protonated merocyanine (M-OH⁺). Kinetic analysis

Department of Chemistry and Biochemistry, Texas State University, 601 University Dr., San Marcos, TX 78666, USA. E-mail: wb20@txstate.edu † Electronic supplementary information (ESI) available: DFT-B3LYP optimized geometries, isomer populations, experimental details, conformer drift times and mass spectra. See DOI: 10.1039/c3cc47697a

also supported SP protonation at the nitrogen to form SP-NH⁺ but this species did not produce MC. Ball and co-workers^{8a} used low-temperature NMR and theory to demonstrate O-protonation of the MC as the dominant process in the presence of acid. Cartesian coordinate input files for CCS calculations were determined from DFT-B3LYP optimized geometries† using the 6-31++G(d,p) basis set. Starting DFT geometries were based on the ground state structures of Sheng and co-workers^{6b} with inclusion of protonation for the MC and SP structures and then optimized to give final calculated structures. These structures remained essentially the same as those determined by Sheng and co-workers, except for the TCC isomer which assumed a conformation better described as the CCT isomer after optimization. Sheng and co-workers did not include the indole methyl groups and suggested that these methyl groups will alter the preferred pathway from an intermediate TCC structure (no methyl groups) to the CCC structure. Optimized geometries used for CCS determination are given in the ESI.[†]

Fig. 1 displays a summary of the IM-MS data. General observations from the IM-MS data include: (1) all SP compounds studied display three peaks corresponding to three isomeric monomers, in order of increasing drift times (t_D) , (2) the percent relative intensity of each peak is dependent on sample treatment, and (3) the difference in drift time between peaks 2 and 3 is 1.4–2.5 times larger than the difference between peaks 1 and 2.

Fig. 2 shows the IM-MS spectra of SP-1 at equilibrium and after irradiation at visible or UV wavelengths. Three singly charged monomer peaks corresponding to SP-1 were identified based on identical isotopic patterns, which clearly showed the existence of discrete isomers instead of a doubly charged dimer or triply charged trimer. Upon irradiation by visible or UV light, the abundance ratio of the isomers changed significantly for SP-1. The same measurements were performed for SP-2 and SP-3 and similar figures are included with the ESI.†

The CCS values, given in Table 1, for each derivative were calculated by MOBCAL using the projection approximation (PA)



Fig. 1 Experimental IM-MS data. Vis, UV, and EQ denotes visible irradiation (>400 nm), UV irradiation (300-400 nm) or equilibrated sample.



Fig. 2 Example of IM-MS data with identical isotopic patterns for singly charged SP-**1** ions, corresponding to isomeric structures. Similar plots for SP-**2** and SP-**3** can be found in the ESI.†

Table 1 MOBCAL collision cross-sections (Å²) of SP's $1\!-\!3$ using projection approximation (PA) and trajectory (TJ) method based on DFT optimized structures

Isomer	SP-1		SP-2		SP-3	
	PA	тј	PA	тј	PA	TJ
SP	113.30	113.27	120.66	122.69	115.54	111.74
CCC	114.63	117.45	122.57	124.13	116.82	114.48
CCT	112.76	113.57	121.50	122.35	114.86	112.78
TTC	119.38	118.55	128.24	127.28	121.54	115.85
CTC	119.71	118.29	128.63	128.27	121.96	116.37
TTT	119.46	117.83	128.33	126.56	121.58	115.38
CTT	119.56	117.97	128.36	127.48	121.82	116.07

and trajectory (TJ) methods.^{13*a*,*b*} It is important to note that the CCSs obtained from modelling were used only qualitatively to determine the relative conformer size for correlation with drift times. MOBCAL uses helium as a buffer gas in CCS determination *via* the TJ method while our experimental data was collected with N₂ buffer gas. This should not significantly affect our analysis because relative size increases are nearly uniform and the size ordering remains qualitatively the same.^{13c}

Specific isomers observed in Fig. 1 were assigned by comparison of the CCSs to experimental drift times (isomer population data is provided as ESI[†]). We assume all isomers have similar ionization efficiency. This comparison also assumes a linear relationship between CCS and t_D . We have omitted TCT in our analysis based on the literature^{6b} and omission of the TCC isomer was based on our DFT optimizations. Thus, the remaining 7 isomers (6 MC isomers and SP) fall into two groups: the SP-CCX isomer group and the XTX isomer group.

We assign peaks 1 and 2, with smaller t_D , to the SP-CCX group. The small difference in theoretical CCS prohibits specific assignment to SP vs. CCX. We assign peak 3 to the XTX isomer group due to its larger CCS. Changes in peak intensity with irradiation support our assignments. For SP-1 and -2, the intensity of peaks 1 and 2 decrease with UV irradiation and increase with subsequent visible exposure in contrast to SP-3 where little change is observed. These observations are consistent

with literature values for the rate of thermal ring-closure (*k*) from MC to SP where: $k(SP-3) \approx 50 \times k(SP-1) \approx 2-6 \times k(SP-2)$.^{2,11b,14} If we use experimental studies in solution as a guide, we speculate that the identity of the XTX isomer is TTC.^{6b}

The assignment of CCX to an intermediate with a lifetime of milliseconds is controversial. Based on transient absorption studies, CCX species have lifetimes well below milliseconds on the photochemical reaction pathway which would make detection difficult under our experimental conditions. However, we note that our observations reflect a system which after initial irradiation, is equilibrating thermally up to the moment of transfer into the gas phase. Our conclusion that we have observed CCX relies on the qualitative comparison of CCS values to experimental drift times because direct quantitative correlation between CCS values and drift times in travelling wave ion mobility is not yet fully understood. Recent experimental studies have argued that biomolecule structure is preserved during the ESI process and the structures largely reflect that in solution.¹⁵ This suggests that dynamic behaviour is temporarily "frozen" when the molecules are transferred from solution (thermodynamically controlled) to gas phase (kinetically controlled). We argue that the solution structure of the SP-MC system is preserved during our experiments and our results provide a unique perspective on this classic photochromic system. Photoisomerization of SP in the gas phase has been studied; ionization potentials were combined with theory but their conclusions did not contradict theoretical results.¹⁶ This gas phase study also built on the work of Sheng and co-workers, which used a reduced atom set for SP.

Based on our results, we conclude that the likely reaction pathway is: SP \rightleftharpoons CCT/CCC \rightleftharpoons TTC/CTC. Theoretical values for the relative energies of the TTC and TTT isomers revealed a minor difference for calculations *in vacuo versus* DCM solution.¹⁷ Based on explicit solvent modeling, Eilmes¹⁸ reported that a few water molecules are sufficient to stabilize MC. Ganesan and Remacle¹⁹ studied the effect of protonation, charge and external electric fields on the SP–MC process. They reported that external fields favour SP ring-opening, but protonation affects reactivity more than external electric fields. We feel our results are reflective of SP–MC dynamics and the contribution of field effects does not alter our conclusions significantly.

Mechanistic elucidation of the elementary steps in SP-MC isomerization has been largely limited to transient spectroscopy and model systems. The combination of ESI with IM-MS provides additional information on the structure-dynamics of this important photochromic system.

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