

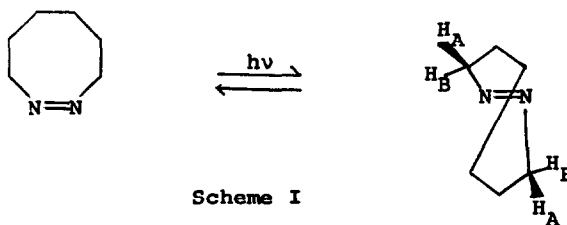
trans-AZO LINKAGES IN EIGHT-, NINE-, AND TEN-MEMBERED CYCLIC AZO COMPOUNDS<sup>1</sup>

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We wish to report the preparations of the first medium-sized cyclic azo compounds possessing trans-azo linkages, namely, trans-1,2-diaza-1-cyclooctene (1), trans-3,8-dimethyl-trans-1,2-diaza-1-cyclooctene (2), trans-1,2-diaza-1-cyclononene (3) and trans-1,2-diaza-1-cyclodecene (4). Irradiation of cis-1,2-diaza-1-cyclooctene (5)<sup>2</sup> for 10 hrs resulted in a 60% conversion to its isomer 1, which was purified by chromatography over Florisil. The photoisomerization,<sup>3</sup> which was shown to be reversible by irradiation of pure 1 (Scheme I), can be followed by nmr. The  $\alpha$ -methylene protons of 5 appear as a triplet at 5.80  $\tau$ , whereas the  $\alpha$ -methylene protons of 1 are magnetically nonequivalent, resulting in multiplets at 5.05 and 6.50 $\tau$ .



The literature oxidation<sup>2</sup> of a mixture of cis- and trans-3,8-dimethyl-1,2-diazacyclooctane with mercuric oxide followed by chromatography over Florisil gave cis-3,8-dimethyl-cis-1,2-diaza-1-cyclooctene (6)<sup>2</sup> and trans-3,8-dimethyl-trans-1,2-diaza-1-cyclooctene (2).<sup>4</sup> That the methyl groups of 2 have a trans configuration was strongly suggested by the equivalence of the methine protons on C-3, which results in a symmetrical sextet at 6.40 $\tau$ . The compounds, 1,2-dicarbethoxy-1,2-diazacyclononane and 1,2-dicarbethoxy-1,2-diazacyclodecane, were prepared in 3 and 9% yields, respectively, by cyclizing the appropriate  $\alpha,\omega$ -dibromides or ditosylates with sym-dicarbethoxyhydrazine. Hydrolysis of the diesters with potassium hydroxide and subsequent oxidation with mercuric

oxide or oxygen afforded 3 and 4 in approximately 50% yields. The structures of all compounds were confirmed by nmr, ir, elemental analyses, and either molecular weight or mass spectral data.

The stereochemistries of the azo linkages are well established by ultraviolet, dipole moment and europium shift data. It has already been demonstrated that ultraviolet absorption maxima of cis-azo compounds usually appear at greater wavelengths than those of trans-azo compounds.<sup>2,5-10</sup> Moreover, cis-azo absorptions are accompanied by larger extinction coefficients.<sup>5,6,8-10</sup> Dipole moments of cis-azo compounds are significantly larger than those of similar compounds containing a trans-azo linkage.<sup>5,7,8</sup> The uv and dipole moment data in Table I clearly allow the assignment of a trans-azo linkage for com-

Table I. Spectral and Dipole Moment Data

Compound	isooctane		$\mu, D$	$\Delta E_u$
	$\lambda_{max}$	$\epsilon$		
<u>1</u>	372	35	1.10	$H_A = 9.0; H_B = 7.5$
<u>2</u>	371	40	0.86	2.3
<u>3</u>	371	60	1.24	5.5
<u>4</u>	368	41	0.64	7.5
<u>5</u>	389	110	3.09	24.0
<u>6</u>	387	128	3.04	11.5

pounds 1-4.

The results of nmr europium shift studies further confirm the azo configurations. The europium complex,  $Eu(fod)_3$ <sup>11,12</sup> was found to coordinate stronger with cis-cyclic azo compounds than with the corresponding trans-isomers. Since the two lone-pair electrons of a cis-azo linkage are orientated on the same side of the molecule, the  $\Delta E_u$  values<sup>13</sup> are somewhat enhanced. The  $\Delta E_u$  values for the  $\alpha$ -methylene or  $\alpha$ -methine protons of compounds 1-6 are presented in Table I. The coordination magnitudes ( $\Delta E_u$ ) were obtained by plotting the observed downfield chemical shifts against the  $Eu(fod)_3$ /substrate molar ratios.<sup>14,15</sup> The significantly larger  $\Delta E_u$  values observed for the cis isomers are consistent with the dipole moment and ultraviolet measurements and demonstrate the

feasibility of this method for determining the azo configuration.

The chemical shifts of the t-butyl groups of  $\text{Eu}(\text{fod})_3$  in the presence of the azo compounds 1-6 are listed in Table II. The stronger coordination at

Table II. The Chemical Shifts ( $\tau$ ,  $\text{CCl}_4$ ) of the t-butyl Protons of  $\text{Eu}(\text{fod})_3$  at a  $\text{Eu}(\text{fod})_3$ /substrate Molar Ratio of 0.10

Compound	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	
$\tau$	8.72	8.5	8.67	8.55	9.35	9.20	8.18 <sup>a</sup>

<sup>a</sup>  $\text{Eu}(\text{fod})_3$  in  $\text{CCl}_4$ .

the cis-azo groups results in a larger upfield shift of the t-butyl protons, which may also be used as a reference of azo coordination power.

Recently, Hart and Love<sup>15</sup> reported that intermolecular competition between different functional groups for a limited quantity of shift reagent can establish a preferred complexation site. Similar intermolecular competition was observed between 1 and 5. When increasing amounts of  $\text{Eu}(\text{fod})_3$  were added to a 3:2 mixture of 1 and 5, the  $\text{H}_A$  and  $\text{H}_B$  protons of 1 remained essentially unaffected by the shift reagent, while the methylene triplet of 5 was gradually shifted downfield. This observation establishes a preferred complexation site at the cis-azo linkage.

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3. A Hanovia medium pressure mercury arc lamp was used for the irradiation which was carried out on samples in nmr tubes at 12-14°C. Only a trace amount (<2%) of nitrogen was evolved.

4. Isomer 2 was previously reported<sup>2</sup> as possessing a cis-azo linkage.
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11. Eu(fod)<sub>3</sub> represents the europium complex with the anion of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.
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13. The  $\Delta E_u$  values represent the downfield shift of particular protons from the chemical shift of the substrate in CCl<sub>4</sub> to the chemical shift which would be observed at equimolar amounts of substrate and shift reagent in CCl<sub>4</sub>. For background information on the determination of  $\Delta E_u$  values consult References 14 and 15.
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