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Bimanes. 25. The Synthesis and Structures of Tricyclic Bimanes (μ-(C_n)-*syn*-(CH_2,CH_3 or Cl)B)

Daniele Marciano,[†] Michel Baud'huin,[†] Baruch Zinger,[†] Israel Goldberg,[†] and Edward M. Kosower*[,†,‡]

Contribution from the Biophysical Organic Chemistry Unit, School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv 69978, Israel, and the Department of Chemistry, State University of New York, Stony Brook, New York 11794-3400.
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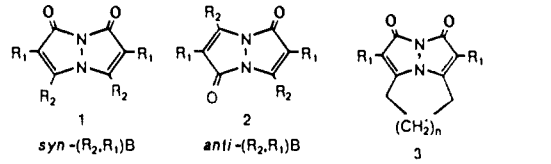
Abstract: An effective synthesis of tricyclic bimanes (μ(C_n)-*syn*-(CH_2,R_1)B, R_1 = CH_3 or Cl)) (**3a–g**, *n* = 1,2,3) from bis-acid chlorides via bis-3-keto esters and bis-pyrazolinones is described. The success of the synthesis is strong support for the previously proposed mechanism of bimane formation, via a diazacyclopentadienone and a diazoketene. Crystal structures for three chloro derivatives (**3b–d**, *n* = 1,2,3) reveal that the bimane dihedral ring angle and crystal packing details vary with the size of the third ring. Other spectroscopic properties (IR, UV, and NMR) vary with dihedral angle.

Introduction

The discovery of a simple synthesis for both *syn*- and *anti*-1,5-diazabicyclo[3.3.0]octadienediones (*syn*- and *anti*-9,10-dioxabimanes (**1** and **2**, respectively), "bimanes") allowed preparation of a variety of these bicyclic systems.[1-3] Bimanes have fascinating chemical,[3-7] photophysical,[8-14] and photochemical properties[15,16] and have found wide use as labeling and thiol analytical agents for biological thiols, proteins, cells, and tissues.[17-32] In order to develop a better understanding of the relationship between the bimane ring–ring dihedral angle[33,34] and photophysical properties, we decided to synthesize and study a series of tricyclic bimanes (**3**, *n* = 0–3).

Derivatives of **3f** (*n* = 1), in which the "bridging" central carbon carries two COOR or CN groups, are readily prepared but cannot be converted into the unsubstituted **3f**.[5] A derivative of **3g** (*n* = 2) with four carbomethoxy groups (**4**) is synthesized with some difficulty from a bis(bromomethyl)bimane (**5**), but is chemically unreactive. We therefore sought a different approach to the synthesis of **3**.



1 *syn*-(R_2,R_1)B

2 *anti*-(R_2,R_1)B

3 μ-$(CH_2)_n$-*syn*-(CH_2,R_1)B

n = 0, **3a**, R_1 = Cl; **3e**, R_1 = CH_3
n = 1, **3b**, R_1 = Cl; **3f**, R_1 = CH_3
n = 2, **3c**, R_1 = Cl; **3g**, R_1 = CH_3
n = 3, **3d**, R_1 = Cl

Using the concept that the two intermediates which react to form bimanes could be generated within the same molecule, we have shown that bis-pyrazolinones could be converted to tricyclic bimanes **3** (*n* = 1–3). In the present article, we describe the synthesis of the tricyclic bimanes **3** (*n* = 1–3), along with the crystal structures of the chloro derivatives **3b**, **3c**, and **3d**. The most strained tricyclic bimanes, **3a** and **3e** (*n* = 0) could be prepared only by the route reported in an accompanying article.[35]

Results

Two general approaches were used for the synthesis of tricyclic bimanes, **3** (*n* = 2). Combination of fragments with suitable bimanes ("fragment addition") was the obvious approach. "Direct synthesis", in which all three rings were created in the same step, was more effective.

Fragment Addition. Formation of μ-(($CH_3OOC)_2C$)-*syn*-(($CH_3OOC)_2CHCH,CH_3$)(CH_2,CH_3)B (6). The bis-bromide, *syn*-(CH_2Br,CH_3)B, bBBr, (**5**) was reacted with excess dimethyl malonate anion, at 5 °C in dry DMF. The tetraester product,

* Author to whom correspondence is to be addressed.
† Tel-Aviv University.
‡ State University of New York, Stony Brook.

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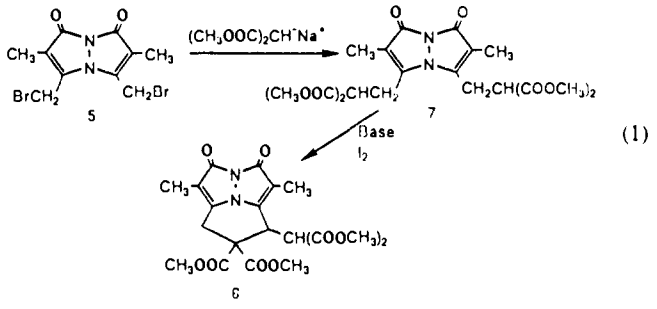
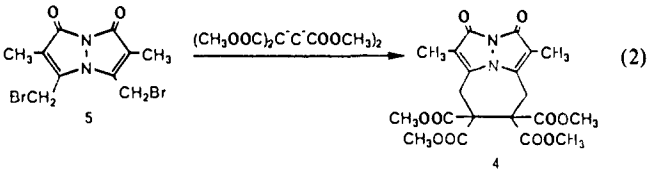
syn-$(CH_3OOC)_2CHCH_2,CH_3)$B (**7**) (*syn*-4,6-(2,2-dicarbomethoxyethyl)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-dien-2,8-dione or 9,10-dioxa-*syn*-(2,2-dicarbomethoxyethyl,methyl)bimane) was not converted to a CH_3-μ-C_2 derivative via oxidative coupling of the dianion with iodine but gave an isomeric compound, **6** (*syn*-4,6-(1,3-(1,1-dicarbomethoxymethyl)-2,2-dicarbomethoxytrimethylene)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione), the structure being assigned on the basis of NMR, mass, and UV spectra. Electrolytic generation of iodine produced a higher yield of **6** than addition of solid iodine to the reaction mixture, (eq 1).



(1)

Synthesis of Tricyclic Tetraester μ-$((CH_3OOC)_2CC(COOCH_3)_2)$-*syn*-$(CH_2,CH_3)$B (4). The conditions required for formation of dimethyl succinate dianion,[36] lithium diisopropylamide in THF at −70 °C, led to destruction, rather than substitution, of bBBr (**5**), presumably because of ring opening. The less basic dianion of tetramethyl 1,1,2,2-ethanetetracarboxylate (from oxidative coupling of dimethyl malonate[37]) was reacted with bBBr (**5**) in DMSO[38] at 10 °C to yield ca.11% of the tricyclic bimane μ-$((CH_3OOC)_2CC(COOCH_3)_2)$-*syn*-$(CH_2,CH_3)$B (**4**) (*syn*-4,6-(1,4-(2,2,3,3-tetracarbomethoxytetramethylene))-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione). Neither acid hydrolysis of the ester groups of **4** nor displacement of carboxyl from methyl groups by iodide succeeded under conditions in which the bimane ring survived (eq 2).

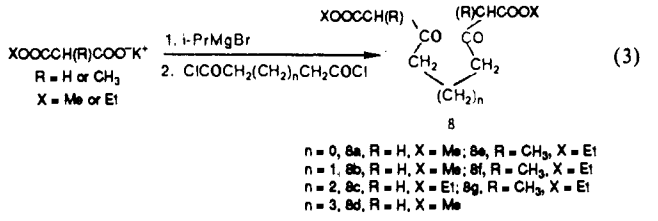


(2)

Direct Synthesis. With a linkage in place between the two pyrazolinone precursors for tricyclic bimanes, an excellent synthesis could be carried out starting with bis-3-keto esters.

Synthesis of Bis-3-keto Esters. Two methods are used to prepare bis-3-keto esters, through reaction of a diacyl chloride either with (a) a suitable malonate derivative or (b) a cyclic ester known as Meldrum's acid. The synthesis from malonate esters could be used to prepare keto esters with different α-substituents and usually gave better yields of purer products.

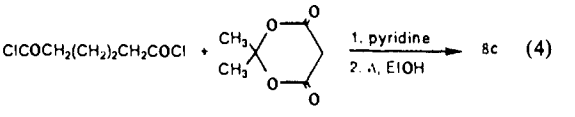
Bis-3-keto Esters by Acylation of Potassium Ethyl 2-Methylmalonate or Potassium Ethyl Malonate. The reaction of isopropyl magnesium bromide with potassium methyl (or ethyl) malonate or potassium ethyl 2-methylmalonate yields the bis-bromomagnesium salts of methyl (or ethyl) hemimalonate or ethyl 2-methylhemimalonate.[39] The latter salts are reacted with glutaryl, adipoyl, or pimeloyl chlorides to produce bis-3-keto esters (**8a–g**) in 64–85% yield, including dimethyl 3,6-dioxooctanedioate (**8a**), dimethyl 3,7-dioxononanedioate (**8b**), diethyl 3,8-dioxodecanedioate (**8c**), dimethyl 3,9-dioxoundecanedioate (**8d**), diethyl 2,7-dimethyl-3,6-dioxooctanedioate (**8e**), diethyl 2,8-dimethyl-3,7-dioxononanedioate (**8f**), and diethyl 2,9-dimethyl-3,8-dioxodecanedioate (**8g**) (eq 3). The synthesis of the bis-3-keto esters



(3)

from the potassium hemimalonate salts is "one pot". A 2-fold excess of the salt over the amount of diacyl chloride is used to promote the formation of the desired bis-derivative. The crude bis-3-keto esters are sufficiently pure to be used for the synthesis of the pyrazolinones.

Bis-3-keto Esters by Acylation of Meldrum's Acid. Reaction of adipoyl chloride with 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid)[40,41] gave a 50% yield of diacylated derivative, which was converted to bis-3-keto ester **8c** by heating in ethanol (eq 4). The method is limited, since (a) 2-substituted bis-3-keto esters cannot be prepared and (b) glutaryl chloride (C_5) and pimeloyl chloride (C_7) failed to give the diacylated derivatives in our hands.



(4)

Synthesis of Bis-pyrazolinones and Bis-chloropyrazolinones. The bis-3-keto esters (**8a–g**) are reacted with hydrazine in hot ethanol to give 45–72% yields of the corresponding bis-pyrazolinones (**9a–g**), 3,3′-dimethylenebis(pyrazol-2-in-5-one) (**9a**), 3,3′-trimethylenebis(pyrazol-2-in-5-one) (**9b**), 3,3′-tetramethylenebis-(pyrazol-2-in-5-one) (**9c**), 3,3′-pentamethylenebis(pyrazol-2-in-5-one) (**9d**), 3,3′-dimethylenebis(4-methylpyrazol-2-in-5-one) (**9e**), 3,3′-trimethylenebis(4-methylpyrazol-2-in-5-one) (**9f**), and 3,3′-tetramethylenebis(4-methylpyrazol-2-in-5-one) (**9g**). The bis-pyrazolinones are rather insoluble solids and are sometimes difficult to characterize. Depending upon solvent, the enol or keto form may be present.[42]

The bis-chloropyrazolinones are solids easily obtained by chlorination of the corresponding pyrazolinone[43,44] and readily identified by ^{1}H NMR spectroscopy. Purification by column chromatography can be used to remove starting materials and products of further chlorination. Reaction of bis-pyrazolinones **9a–g** with chlorine in dichloromethane at room temperature affords the corresponding dichloro- or tetrachloropyrazolinones in 64–100% yield. The tetrachloropyrazolinones arise from the keto esters derived from potassium methyl malonate or Meldrum's acid and are 3,3′-dimethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10a**), 3,3′-trimethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10b**),

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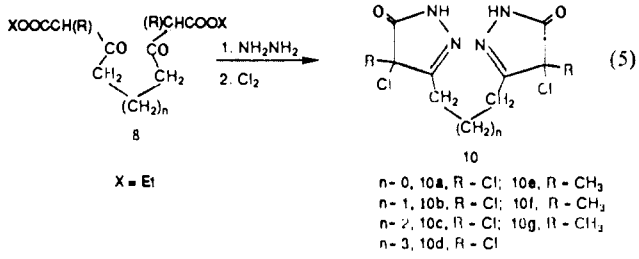
Table I. Yields of Intermediates and Tricyclic Bimanes (R-μ-C_n) (Yields, %)

bridge n	bis-keto ester	pyrazolinone	chloropyrazolinone	bimane	overall yield (%)
		R = Cl			
0	**8a** (80)	**9a** (65)	**10a** (100)	**3a** (–)	
1	**8b** (64)	**9b** (45)	**10b** (75)	**3b** (65)	14
2	**8c** (85)	**9c** (60)	**10c** (80)	**3c** (90)	36
3	**8d** (82)	**9d** (72)	**10d** (72)	**3d** (24)	10
		R = CH_3			
0	**8e** (97)	**9e** (92)	**10e** (99)	**3e** (–)	
1	**8f** (81)	**9f** (67)	**10f** (64)	**3f** (30)	10
2	**8g** (76)	**9g** (60)	**10g** (100)	**3g** (92)	42

3,3′-tetramethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10c**), and 3,3′-pentamethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10d**). The dichloropyrazolinones are 3,3′-dimethylenebis(4-chloro-4-methylpyrazol-2-in-5-one) (**10e**), 3,3′-trimethylenebis(4-chloro-4-methylpyrazol-2-in-5-one) (**10f**), and 3,3′-tetramethylenebis-(4-chloro-4-methylpyrazol-2-in-5-one) (**10g**) (eq 5). These final precursors to the bimanes can usually be prepared in a state of high purity.

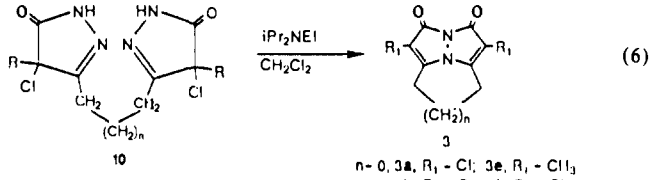


8 10 (5)

X = Et

n = 0, 10a, R = Cl; 10e, R = CH_3
n = 1, 10b, R = Cl; 10f, R = CH_3
n = 2, 10c, R = Cl; 10g, R = CH_3
n = 3, 10d, R = Cl

Synthesis of Tricyclic Bimanes. The tricyclic bimanes (**3**) are formed by the base-catalyzed cyclization of the bis-chloropyrazolinones (**10**). At least one of the starting reactants must be soluble. The bis-chloropyrazolinones are insoluble in CH_2Cl_2 and since $K_2CO_3 \cdot {}^3/_2H_2O$ is also insoluble, the "classical" *syn*-bimane synthesis using the "heterogeneous procedure" was not successful. Diisopropyl ethylamine (Hünig's base) is soluble, strong enough to eliminate HCl from a chloropyrazolinone, and hindered enough not to attack the carbonyl group. Dichloro- or tetrachloropyrazolinones (**10a–g**) are treated at room temperature with diisopropylethylamine to produce the tricyclic *syn*-bimanes Cl-μ-C_1 (**3b**), Cl-μ-C_2 (**3c**), Cl-μ-C_3 (**3d**), CH_3-μ-C_1 (**3f**), and CH_3-μ-C_2 (**3g**) in 30–92% yield. The best yields were obtained for compounds with seven-membered third rings, 92% for CH_3-μ-C_2 (**3g**) and 90% for Cl-μ-C_2 (**3c**). The tricyclic bimanes, all yellow solids, are Cl-μ-C_1, 4,6-(1,3-trimethylene)-3,7-dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3b**); Cl-μ-C_2, 4,6-(1,4-tetramethylene)-3,7-dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3c**); Cl-μ-C_3, 4,6-(1,5-pentamethylene)-3,7-dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3d**); CH_3-μ-C_1, 4,6-(1,3-trimethylene)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3f**); and CH_3-μ-C_2, 4,6-(1,4-tetramethylene)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione (**3g**) (eq 6). Table I summarizes the results of the syntheses.



10 3 (6)

n = 0, 3a, R_1 = Cl; 3e, R_1 = CH_3
n = 1, 3b, R_1 = Cl; 3f, R_1 = CH_3
n = 2, 3c, R_1 = Cl; 3g, R_1 = CH_3
n = 3, 3d, R_1 = Cl

Physical Properties of Tricyclic Bimanes. The thermal stability of most of the tricyclic bimanes is shown by the fact that CH_3-μ-C_n and Cl-μ-C_n melt between 225 and 247 °C without decomposition,

Table II. Physical Properties of the Tricyclic Bimanes (**3a–g**)

	UV (CH_3CN): λ_{max}, nm	IR(KBr) (C=O): ν, cm^{-1}	fluorescence spectrum (CH_3CN): λ_{max}, nm (ϕ_F)	crystal density: g cm^{-3}
CH_3-μ-0 (**3e**)	315	1770	448 (0.75)	1.430
CH_3-μ-C_1 (**3f**)	334	1750	440 (0.33)	
CH_3-μ-C_2 (**3g**)	366	1746	440 (0.68)	
Cl-μ-0 (**3a**)	324	1762	444 (0.2)	
Cl-μ-C_1 (**3b**)	346	1775	442 (0.52)	1.705
Cl-μ-C_2 (**3c**)	374	1770	444 (0.86)	1.591
Cl-μ-C_3 (**3d**)	375	1765	420 (0.40)	1.562

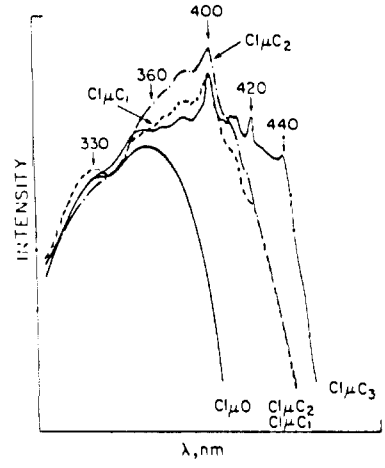


Figure 1. The excitation spectra of crystalline bimanes at room temperature with emission at 465 nm. The absorption maxima in CH_3CN solution are given for comparison. The bimanes include Cl-μ-0 (**3a**), 324 nm; Cl-μ-C_1 (**3b**), 346 nm; Cl-μ-C_2 (**3c**), 374 nm; Cl-μ-C_3 (**3d**) 375 nm.

except for Cl-μ-C_2 (**3c**), which partly decomposes to give unidentified nonfluorescent materials. Some of the physical properties of the tricyclic bimanes (**3a–g**) are summarized in Table II.

Ultraviolet Absorption Spectra. The ultraviolet absorption maxima for the chloro-substituted tricyclic bimanes in CH_3CN shift from 346 to 374 to 375 nm as the exobimane ring size changes from six atoms in Cl-μ-C_1 (**3b**) to seven atoms in Cl-μ-C_2 (**3c**) to eight atoms in Cl-μ-C_3 (**3d**). For methyl-substituted tricyclic bimanes, the maxima are 334 nm for CH_3-μ-C_1 (**3f**) and 366 nm for CH_3-μ-C_2 (**3g**). The tricyclic bimanes substituted with chlorine absorb at longer wavelengths than the corresponding methyl-substituted tricyclic bimanes.

Infrared Absorption Spectra. The carbonyl absorption moves to longer wavelengths as the bridge becomes longer, i.e., as the system becomes less strained. For the chloro-substituted tricyclic bimanes, the maximum is at 1775 cm^{-1} for Cl-μ-C_1, 1770 cm^{-1} for Cl-μ-C_2, 1765 cm^{-1} for Cl-μ-C_3. The carbonyl band for the methyl-substituted bridged compounds is found at longer wavelengths, but shows changes parallel to the chloro derivatives with bands at 1750 cm^{-1} for CH_3-μ-C_1 and at 1746 cm^{-1} for CH_3-μ-C_2.

Fluorescence Emission Spectra. All the carbon-bridged tricyclic bimanes exhibit fluorescence emission spectra in CH_3CN which vary very little with structure, with a maximum at 440 nm and a shoulder at 460 nm. The chloro-substituted tricyclic bimanes have somewhat higher quantum yields of fluorescence than the corresponding methyl-substituted derivatives, in contrast to bimanes without a bridge. The fluorescence emission spectra of the crystalline bimanes could be obtained by front face excitation. Except for CH_3-μ-C_1 (**3f**), which emits at the same wavelength from the solid and solution, emission from the solid was shifted in all the other compounds to the red by 25 nm (λ_{max} 465 nm with a shoulder at 480 nm).

Fluorescence Excitation Spectra. The excitation maxima for the fluorescence of the tricyclic bimanes in acetonitrile (380 nm) are at longer wavelengths than the absorption maxima (340 nm). The excitation maxima (emission at 465 nm) at room temperature are at 400 nm for most of the crystalline tricyclic bimanes. The larger is the exobimane ring, the more important are the shoulders

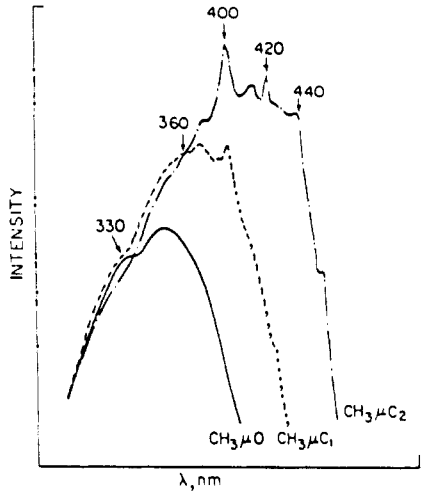


Figure 2. The excitation spectra of crystalline bimanes at room temperature with emission at 465 nm. The absorption maxima in CH_3CN solution are given for comparison. The bimanes include CH_3-μ-0 (**3e**), 315 nm; CH_3-μ-C_1 (**3f**), 334 nm; CH_3-μ-C_2 (**3g**), 366 nm.

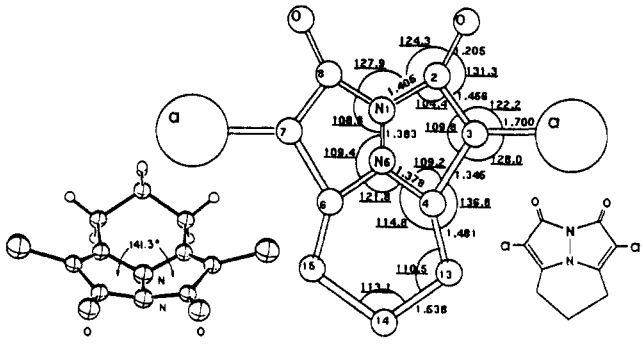


Figure 3. Bond distances (estimated standard deviation 0.002–0.003 Å) and angles (estimated standard deviation 0.1–0.2°) for μ-(C1)-*syn*-(CH_2,Cl)B. A view of the crystal structure is shown together with the chemical formula.

at longer wavelength, resulting in an overall red-shift of the excitation spectrum (Figures 1 and 2).

^{1}H NMR Spectra. The chemical shifts of protons on the methylene adjacent to the bimane rings, 2.91 ppm for Cl-μ-C_1, 2.98 ppm for Cl-μ-C_2, and 3.01 ppm for Cl-μ-C_3, are influenced a little by the size of the bridge and are shifted to higher fields in 3,7-methyl-substituted tricyclic bimanes, with shifts at 2.83 ppm in CH_3-μ-C_2 and 2.75 ppm in CH_3-μ-C_1.

^{13}C NMR Spectra. The chemical shifts of the carbonyl carbons, 157 ppm in Cl-μ-C_1, 155 ppm in Cl-μ-C_2, and in Cl-μ-C_3 are not affected much by the size of the exobimane ring. The signal shifts to 163 ppm in CH_3-μ-C_1 and 161 ppm in CH_3-μ-C_2.

Crystal Structure Analysis of Cl-μ-C_1, Cl-μ-C_2, Cl-μ-C_3. Single crystals of Cl-μ-C_1 and of Cl-μ-C_3 were obtained from methylene chloride solutions or, in the case of Cl-μ-C_2, from ethyl acetate by slow evaporation. The methyl-substituted tricyclic bimanes CH_3-μ-C_2 and CH_3-μ-C_1 form, from all solvents tried, twinned crystals unsuitable for structure determination. The crystal data are as follows: Cl-μ-C_1, a = 16.096 (4), b = 8.415 (1), c = 7.175 (5) Å, β = 100.76 (3)°, space group *Cc*, D_c (g cm^{-3}) = 1.7049 for Z = 4; Cl-μ-C_2, a = 6.902 (2), b = 14.849 (2), c = 17.490 (3) Å, α = 64.88 (1), β = 88.51 (2), γ = 89.97 (2)°, space group $P\bar{1}$, D_c (g cm^{-3}) = 1.5910 for Z = 6; Cl-μ-C_3, a = 7.970 (4), b = 12.080 (4), c = 12.223 (3) Å, β = 99.33 (3)°, space group $P2_1/c$, D_c (g cm^{-3}) = 1.5622 for Z = 4.

Details on the X-ray measurements and the crystal structure refinements are given in the Experimental Section. The final atomic parameters for Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3 are given in Tables III–V, respectively; these tables and a summary of intramolecular and intermolecular distances as well as the principal components of the atomic thermal parameters has been deposited

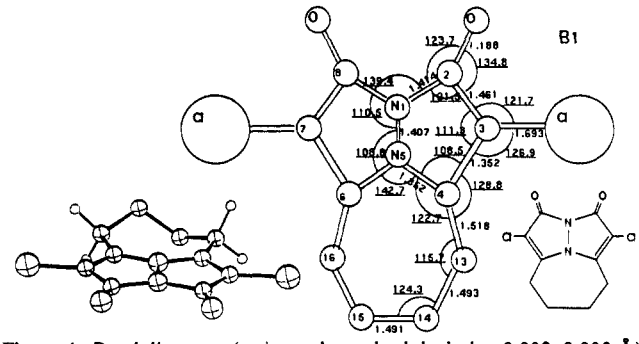


Figure 4. Bond distances (estimated standard deviation 0.002–0.003 Å) and angles (estimated standard deviation 0.1–0.2°) for the B1 form of μ-(C2)-*syn*-(CH_2,Cl)B. A view of the crystal structure is shown together with the chemical formula.

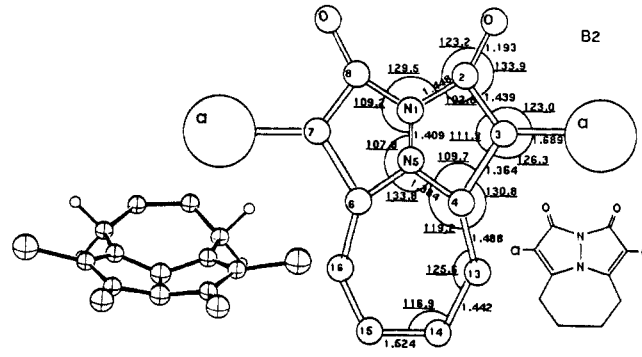


Figure 5. Bond distances (estimated standard deviation 0.002–0.003 Å) and angles (estimated standard deviation 0.1–0.2°) for the B2 form of μ-(C2)-*syn*-(CH_2,Cl)B. A view of the crystal structure is shown together with the chemical formula.

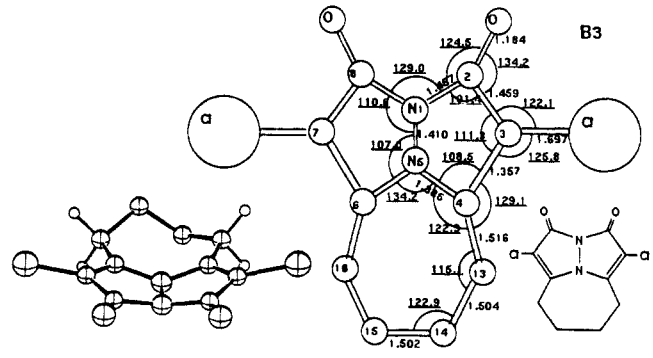


Figure 6. Bond distances (estimated standard deviation 0.002–0.003 Å) and angles (estimated standard deviation 0.1–0.2°) for the B3 form of μ-(C2)-*syn*-(CH_2,Cl)B. A view of the crystal structure is shown together with the chemical formula.

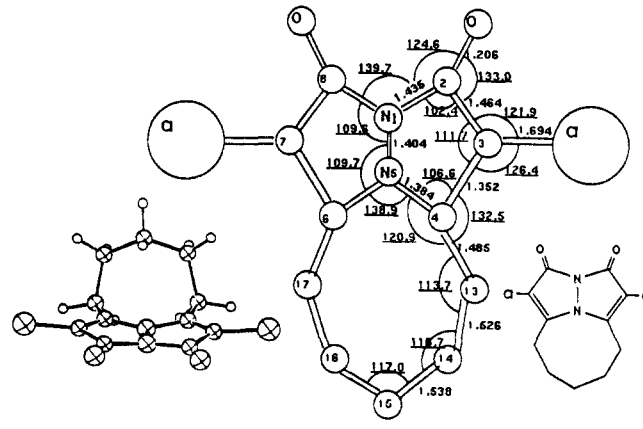
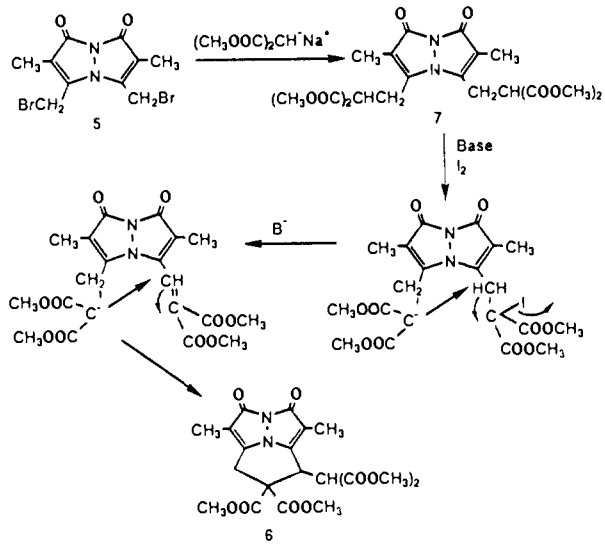


Figure 7. Bond distances (estimated standard deviation 0.002–0.003 Å) and angles (estimated standard deviation 0.1–0.2°) for μ-(C3)-*syn*-(CH_2,Cl)B. A view of the crystal structure is shown together with the chemical formula.

Scheme I. Mechanism for Formation of the Tricyclic Bimane **6**



as supplementary material (Tables III–IX). The observed molecular structures along with atom numbering are shown in Figures 3–7. Cl-μ-C_1 crystallizes with one molecule in the asymmetric unit. The dihedral angle between the two five-membered rings is 141°. Cl-μ-C_2 crystallizes with three molecules of different conformation in the same asymmetric unit. The dihedral angles are for molecule B1, 180°; for molecule B2, 150°; and for molecule B3, 151°. Cl-μ-C_3 crystallizes with one molecule in the asymmetric unit, the dihedral angle being 169°. In all three compounds, the individual five-membered rings are found to be almost planar (Figures 3–7).

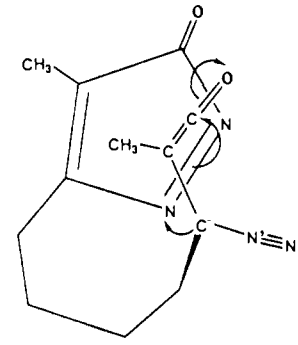
Discussion

Synthesis. Fragment addition was an attractive route for the preparation of tricyclic bimanes because of the ready availability of suitable reactive bimanes and appropriate nucleophiles. Substituted six, seven, and eight-membered tricyclic bimanes could indeed be made in this way, but no simple method was found for preparing the unsubstituted tricyclic bimanes. In addition, the yields of the least substituted products were not especially high. The "fragment addition" method was not attempted with the precursors to chloro-substituted tricyclic bimanes, *syn*-(CH_2Br,Cl)B and *syn*-(CH_2=CH,Cl)B, since these were not available until we had almost completed the present research.

Formation of a Six- or an Eight-Membered Ring by "Fragment Addition". The carboxylic acid substituted tricyclic bimane with a six-membered ring, μ-(HCCOOH)-*syn*-(CH_2,CH_3)B, derived via **6** from *syn*-(CH_2Br,CH_3)B (**5**) and diethyl malonate, is obtained in low overall yield (8.6%);[4] CH_3-μ-C_1 could not be obtained by decarboxylation. The carboxylic acid substituted tricyclic bimane with a eight-membered ring, μ-(CH_2(HOOC)-CHCH_2)-*syn*-(CH_2,CH_3)B derived from *syn*-(CH_2=CH,CH_3)B and diethyl malonate was obtained in 40% yield (9.5% from *syn*-(CH_3CHBr,CH_3)B); CH_3-μ-C_3 was not obtained by decarboxylation.[3] In both cases, there is little driving force for the loss of carbon dioxide from a carboxylic acid attached to the central carbon of the bridge. The mechanism of formation of the tricyclic **6** can be explained by the sequence shown in Scheme I. The initial reactions are abstraction of a proton and formation of an α-iodo derivative. An anion is then produced by abstraction of a proton. Rather than displace iodide from the sterically hindered tertiary position, the anion abstracts a proton to eliminate HI, forming an α,β-unsaturated ester. Formation of the six-membered ring then occurs by nucleophilic addition.

Formation of a Seven-Membered Ring by "Fragment Addition". The synthesis of the first tricyclic bimane having a seven-membered ring was accomplished with double nucleophilic substitution by the dianion of tetramethyl 1,1,2,2-ethanetetracarboxylate on bBBr (**5**) (eq 2). The yield of the tricyclic μ-(($CH_3OOC)_2$CC-($COOCH_3$)$_2$)-*syn*-(CH_2,CH_3)B (**4**) was 11%. The procedure is not very convenient and gives even lower yields when scaled up. In addition, the tetraester (**4**) resisted acid hydrolysis or displacement of carboxyl from the methyl group by iodide, rendering the "fragment addition" approach ineffective for the preparation of the parent tricyclic. At this point, a different approach was required.

Scheme II. Transition State for Formation of Tricyclic Bimane Intermediate (See Scheme III)



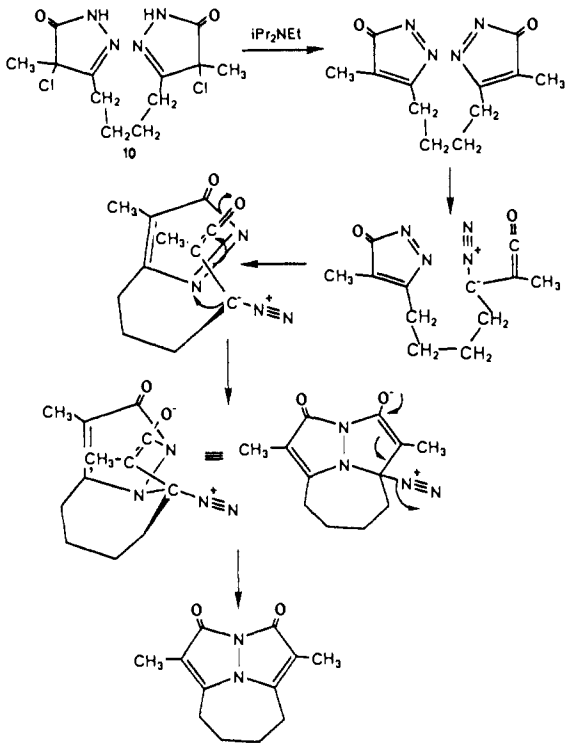
"Direct Synthesis" of Tricyclic Bimanes (CH_3-μ-C_n (n = 1,2) and Cl-μ-C_n (n = 1–3)). On the basis of the mechanism[1] for the formation of bimanes from a diazacyclopentadienone (DC) and a diazoalkylketene derived from DC, we reasoned that connecting the reactive moieties might favor bimane formation. A bridge incorporated into a bis-chloropyrazolinone would lead to the generation of the reactive moieties in proximity to one another, and might facilitate formation of the tricyclic bimanes. We then developed the "direct synthesis" of tricyclic bimanes, which can be summarized in the following steps: bis-acyl chloride → bis-keto esters → bis-pyrazolinones → bis-chloropyrazolinones → tricyclic bimanes. All of the steps of the direct synthesis can be performed on a relatively large scale, with 50–86 mmol of bis-acyl chloride leading to 10–60 mmol of tricyclic bimane, and the reactions are fairly easy to execute.

The relatively high yields obtained in the tricyclic bimane synthesis must be due to the high local concentration of both required intermediates. In the best cases, intermolecular reactions leading to polymers are minimized. It is obvious that for steric reasons no *anti*-bimanes are formed in these reactions. The highest yields are obtained for the seven-membered ring tricyclics, **3g** and **3c**. The initial combination is favored by an appropriate juxtaposition of the two intermediate species linked together by four methylene groups. A plausible transition state (Scheme II) is based on the mechanism previously proposed for the formation of dioxabimanes,[1] in which 2,3-diazacyclopentadienone opens to a diazoalkylketene. The anionic center of the latter adds 1,4 to the diazadienone to yield an intermediate. The latter cyclizes by the attack of a nitrogen anion on the ketene carbonyl, yielding an intermediate which loses nitrogen to form the syn-cyclic product (Scheme III).

Physical Properties of Tricyclic Bimanes. Bimanes have an unusual combination of attributes, most notably in being both *flexible and fluorescent*. The expected difference between the flexibility of the ground and excited states is most clear in the rates of conformational change, ca. 10^6 s^{-1} for the former and 10^{11} s^{-1} for the latter.[12,35] The bridge between the α-carbons of the R_2 groups in bimanes restricts motion and should thus decrease flexibility. The physical and chemical properties of the tricyclic bimanes provide insights into the behavior of all bimanes, especially the complexities introduced by conformational mobility. We consider the crystal structures of a series of tricyclic bimanes of increasing bridge length, and make some comments about absorption and emission spectra.

Crystal Structure Analysis of Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3. Previous structural studies suggested[33] that the simplest bimanes like *syn*-(CH_3,H)B and *syn*-(CH_3,CH_3)B were planar, while more complex bimanes, e.g., *syn*-(C_6H_5,Cl)B, dihedral angle of 172°, were not. Bimanes with one-atom bridges have been found to be folded (the six-membered ring has a chair-like conformation), e.g.,

Scheme III. Mechanism for Formation of Tricyclic Bimanes from Bis-pyrazolinones



μ-(S)-*syn*-(CH_2,CH_3)B, 142°; μ-(($CN)_2$C)-*syn*-(CH_2,CH_3)B, 139°; μ-(SO_2)-*syn*-(CH_2,CH_3)B, 139°. Among the new tricyclic bimanes, Cl-μ-C_1 (six-membered ring) has a dihedral angle of 141.3°. Thus, replacing a sulfur atom by a methylene group does not affect very much the "folding" of the bimane. The longer bridge in Cl-μ-C_2 leads to a more complex outcome, with three different molecules (B_1, B_2, and B_3) in the asymmetric unit. The dihedral angles of B_2 and B_3 are similar and of the expected magnitude, 149.8° and 150.8°, but B_1 is dramatically different, being planar with a dihedral angle of 179.7°. Both bent and planar conformers are present in one molecule in crystals of a bis-*syn*,*syn*-bimane derivative,[33] one bimane being planar (dihedral angle 178°) and the other bent (dihedral angle 153°). The still longer bridge in Cl-μ-C_3 allows the bimane to be more planar (dihedral angle 169.5°). The "zero-bridged" bimane, μ-0-*syn*-(CH_2,CH_3)B (**3e**), has a dihedral angle of 129°, the smallest yet found among the bimanes.[35] The individual five-membered rings deviate only slightly (<0.1 Å) from planarity in all the Cl-μ-C_n molecules.

The flexibility of bimanes is reflected in the thermal parameters of the nitrogen atoms, which show that nitrogen motions normal to the bimane "mean" plane are greater than in other directions (Table 8, supplementary material). The anisotropicity of the thermal parameters for the nitrogens may also imply that the crystallographic results represent the average of (at least) two nonplanar equilibrium forms of the bimane molecule.

Intramolecular Distances and Conjugation. There are five different bond types, C—C, C=C, C=O, N—C, and N—N, in the 9,10-dioxabimane molecule. All carbons are formally sp^2 hybridized, while the N hybridization is formally sp^x in which $x = 2$ in planar molecules and $x > 2$ in bent bimanes.

The nitrogen–nitrogen bond length (N_1–N_5 in numbered formula) is 1.40 Å for the three tricyclic bimanes Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3, a value close to that found for μ-(S)-*syn*-(CH_2,CH_3)B (1.403 Å), as well as to the 1.392 Å N–N bond length in the noncyclic N,N′-diformylhydrazine, OCHNHNHCHO.[47] The N–N bond lengths in 3-pyrazolin-5-ones cluster around 1.39–1.40 Å.[48-51]

The N—C(=O) bond distances in Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3, of 1.43 Å are somewhat longer than the N—C(=C) bond length of 1.38 Å. A comparable mean bond length of 1.42 Å[52] (range 1.397–1.431 Å) of N—C(=O) bond lengths has been found for 1,6-diazabicyclo[4.4.0]cyclodecadienedione.

Although one may estimate bond orders around the central N–N and N–C bonds from the bond lengths according to Burke and Laing,[53] these may not be accurate for constrained, dynamic five-membered ring systems. The N—N and N—C(=O) bond orders are above 1.0 for Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3 while bond orders for N—C(=C) are above 1.25, with the sum around the N5 in the bimanes greater than 3.0, implying some delocalization of the nitrogen nonbonding electrons.

The C=C bond distances average 1.35 Å in Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3, as found in other syn-bimanes. The (C=)C—C(=O) bond distances average 1.46 Å in Cl-μ-C_1, Cl-μ-C_2, and Cl-μ-C_3, slightly shorter than the characteristic $C(sp^2)$–$C(sp^2)$ bond length (1.48 Å) in a quinone.[54] The C=O bond lengths are between 1.18 and 1.20 Å for Cl-μ-C_n, slightly below the average values found for other bridged bimanes, 1.21 Å. The average C–Cl bond length is 1.70 Å for all Cl-μ-C_n compounds and *syn*-(H,Cl)B.

Intermolecular Arrangements. The density of the crystals increases with decreasing bimane dihedral angle, being 1.562 g cm^{-3} for Cl-μ-C_3, 1.591 g cm^{-3} in Cl-μ-C_2, and 1.705 g cm^{-3} in Cl-μ-C_1, reflecting to some extent the looser molecular packing in crystals of bimanes with longer bridges. The densities of Cl-μ-C_n bimanes are greater than the density of a tricyclic bimane with $R_1 = CH_3$ and a larger atom, sulfur, in the bridge, e.g., d_c = 1.45 g cm^{-3} for μ-(S)-*syn*-(CH_2,CH_3)B, but lower than that of the dense *syn*-(H,Cl)B (d_c = 1.863 g cm^{-3}).[55]

The densities of tricyclic bimanes stem partly from intermolecular contacts, with efficiently packed structures in the space groups *Cc* for Cl-μ-C_1, $P\bar{1}$ for Cl-μ-C_2, and $P2_1/c$ for Cl-μ-C_3. Within the molecular layers are somewhat short CH···O van der Waals contacts like one of 2.45 Å in Cl-μ-C_3 (Table 9, supplementary material) although the sum of van der Waals radii of H (1.1 Å) and O (1.40 Å) is 2.50 Å. The donor carbons are bridge methylenes and the acceptors are the carbonyl oxygens.

The shortest chlorine nonbonding distances are those for Cl(11)···Cl(12), 3.44 Å, in Cl-μ-C_2 and H(14)···Cl(12), 3.01 Å, in Cl-μ-C_3, less than the sum of the van der Waals radii, 3.60 Å, for two chlorines and 3.02 Å for nonbonding interaction, H···Cl. The hydrogens belong to the bridge methylene groups.

Conclusions. The symmetrical, cyclic nature of bimanes suggests, at first sight, conjugation and planarity. However, on the basis of the normal bond lengths and ring–ring dihedral angles (<180°) in bimanes, all indications are that delocalization in the ground state is modest. The nonbonding pairs on the nitrogens normally seek arrangements in which overlap is avoided, as in the case of cyclic hydrazines.[56] Delocalization into the carbonyl

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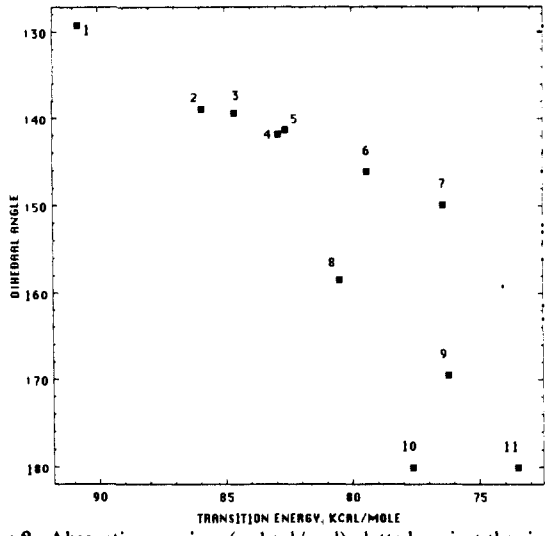

Figure 8. Absorption maxima (as kcal/mol) plotted against the ring–ring dihedral angle found in the crystal. The points represent **1**, μ-O-*syn*-(CH_2,CH_3)B; **2**, μ-(SO_2)-*syn*-(CH_2,CH_3)B; **3**, μ-($C(CN)_2$)-*syn*-(CH_2,CH_3)B; **4**, μ-(Cl)-*syn*-(CH_2,Cl)B; **5**, μ-(S)-*syn*-(CH_2,CH_3)B; **6**, μ-(S)-*syn*-(CH_2,Cl)B; **7**, μ-(C2)-*syn*-(CH_2,Cl)B; **8**, μ-(CH_2SCH_2)-*syn*-(CH_2,CH_3)B; **9**, μ-(C3)-*syn*-(CH_2,Cl)B; **10**, *syn*-(CH_3,CH_3)B; **11**, *syn*-(H,Cl)B. The relationship is quite useful in deriving dihedral angles from the absorption maxima.

groups is limited by the amount of charge built up on adjacent nitrogens. Planarity may be a somewhat misleading structural feature in view of the fact that the thermal parameters for the central nitrogens are considerably greater in the direction normal to the molecular plane than in other directions. The crystallographic structures may thus represent the average of (at least) two nonplanar forms.

Physical Properties of Tricyclic Bimanes Related to Structure

Ultraviolet Absorption and Excitation Spectra. The shift to longer wavelengths of the light absorption maximum of bimanes in solution with increasing ring–ring dihedral angle of tricyclic bimanes confirms in a clear way that bimane folding in solution is related to that in the crystal. Crystal packing forces thus change the folding of the bimane in a consistent way.

Detailed photophysical studies have suggested that emitting states of bimanes are bent in nonpolar solvents and quasiplanar[12] in polar solvents. The fluorescence spectra in solution of ground-state "planar" and "bent" bridged bimanes are quite similar, implying that the bimane rings adopt an excited-state conformation without much constraint from the bridge. The fluorescence maximum of "zero-bridged" bimane **3e** is at wavelengths slightly longer than those of the other tricyclic bimanes.[35]

The excitation maximum for many bimanes in solution is located at wavelengths 10–15 nm longer than the absorption maximum; a larger difference, 25–66 nm, is found for crystals, suggesting that bimanes are more planar in crystals. The more planar the bimane, the more structured the excitation spectrum. Planarity restricts the number of vibrational levels in the ground state and leads to a more structured absorption spectrum, in this case, being detected as the excitation spectrum (Figures 1 and 2). The absorption energies, E_a (kcal/mol) = 28 590/λ_{max} nm), for bimanes are correlated in a striking way with the dihedral angle between the two five-membered rings in crystals (Table 6, Figure 8). The relationship might be taken as showing that the maximum is not too sensitive to small changes in dihedral angle (<25°) but with greater changes, decreases substantially in a way linearly related to the angle. The relationship based on the data summarized in Table 6 (supplementary material) provides a very useful method for assigning dihedral angles from the absorption maximum; it is likely, for example, that *syn*-(CH_3,CH_3)B has a maximum at shorter wavelengths than anticipated from its dihedral angle in the crystal because the molecule is bent in solution.

Although we could not obtain the structures for CH_3-μ-C_1 and CH_3-μ-C_2, due to the lack of suitable crystals, such structures would be of interest since the UV absorption maxima for the methyl derivatives are at shorter wavelengths than those of the corresponding chloro compounds. In the one case for which a direct comparison may be made, the maximum for CH_3-μ-(S) in solution is at 345 nm, with a crystal dihedral angle of 142°. The maximum for Cl-μ-(S) is at 360 nm, with a crystal dihedral angle of 146°.[35] We thus can infer that the dihedral angles for the CH_3-μ-C_n derivatives should be smaller than those found in the crystal structures of the Cl-μ-C_n compounds.

Experimental Section

General. Instruments used are ^{1}H NMR spectra, (chemical shifts in δ values referred to (CH_3)$_4$Si = 0.00) Bruker WH-90 and AM-360 spectrometers; ultraviolet–visible spectra, Cary Model 17 spectrophotometer; fluorescence spectra, Hitachi Perkin-Elmer MPF-4 fluorescence spectrometer; mass spectra, DuPont 21-491B mass spectrometer; IR spectra, Perkin-Elmer Model 177 spectrophotometer; HPLC, Waters Associates Model 6.

Solvents and Materials. Dichloromethane, acetonitrile, and ethyl acetate (Anal.) were used without further purification. Dimethylformamide (DMF) was dried by refluxing over calcium hydride. Dimethyl sulfoxide (DMSO) was dried by refluxing over calcium hydride. Tetrahydrofuran (THF) was distilled from the sodium ketyl of benzophenone. Absorption and emission spectra were measured in Spectrograde acetonitrile or dioxane.

Crystal Structure Analysis. Diffraction data were measured at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator, employing Mo Kα radiation (λ_{mean} = 0.710 69 Å).

The intensities of all reflections with $1 < \theta < 27°$ were recorded by using an $\omega - 2\theta$ scan technique with a varying scan angle of 0.9 + 0.3 tan θ. The scan rate varied according to the detected intensity between 1.0 and 4° min^{-1}. Possible deterioration of the crystals under examination was tested by frequent measurement of the intensities of standard reflections and found to be negligible. The data were not corrected for absorption and extinction effects. Final refinement of the corresponding structural models was based only on those observations that satisfied the condition $F_o^2 > 3\sigma(F_o^2)$.

The crystal structures were solved by a combination of direct methods and Fourier technique (MULTAN).[45] The refinements were carried out by full-matrix least-squares methods including positional and anisotropic thermal parameters of all the non-hydrogen atoms. All hydrogen were calculated at an intermediate stage of the refinement and were assigned isotropic temperature factors. The final R values at convergence are as follows: Cl-μ-C_1, R = 0.044 for 901 observations; Cl-μ-C_2, R = 0.096 for 2530 reflections (the C_2 bridges in the three molecules are partially disordered); Cl-μ-C_3, R = 0.050.

Syntheses. *syn*-(CH_3OOC)$_2$$CHCH_2$,$CH_3$)B (4,6-(2,2-Dicarbomethoxyethyl)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione or 9,10-Dioxa-*syn*-(2,2-dicarbomethoxyethyl,methyl)bimane) (7). Dimethyl malonate (264 mg, 2 mmol) in dry DMF (10 mL) was stirred with NaH (120 mg, 2 mmol, 60% in oil) at −5 °C for 15 min. A solution of *syn*-(CH_2Br,CH_3)B (**5**) (350 mg, 1 mmol) in dry DMF was added dropwise to the malonate salt. The bromo derivative was consumed within 15 min after which the reaction mixture was brought to pH 4 with 0.1 N HCl, the solvent removed under reduced pressure, and the residue chromatographed on silica gel. Elution with dichloromethane/ethyl acetate (1:1) afforded *syn*-((CH_3OOC)$_2$$CHCH_2$,$CH_3$)B (**7**): 175 mg (40% yield); yellow crystals from *i*-PrOH; mp 125 °C; IR (KBr) 3030–2800, 1745, 1735, 1725, 1665, 1630, 1600, 1450, 1430, 1400, 1380, 1280, 1250, 1230, 1200, 1160, 1070, 1050, 1025, 950, 920, 850, 780, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.72 (3 H, s), 3.27 (2 H, d, J = 6 Hz), 3.67 (s, 6 H), 3.67 (t, 1 H, J = 6 Hz) ppm; UV (CH_3CN) λ_{max} 365 nm (ϵ 5140), 250 sh (6100), 232 (15 400); fluorescence maxima (CH_3CN) 435 nm, 460 sh (Φ_F 0.83); mass spectrum m/e 452 (M^+).

μ-((CH_3OOC)$_2$C)-*syn*-((CH_3OOC)$_2$$CHCH$,$CH_3$)($CH_2$,$CH_3$)B (4,6-(1,3-(1,1-Dicarbomethoxymethyl)-2,2-dicarbomethoxytrimethylene)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione) (6). Method A.

(57) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed; University Science Books: Mill Valley, CA, 1980; p 276.
(58) Taylor, E. C.; Turchi, I. J. *Org. Prep. Proced. Int.* **1978**, *10*(5), 221.
(59) The nomenclature (9,10-dioxa-*syn*-bimanes, 4,6-bridged- (or μ-) 9,10-dioxa-*syn*-bimanes, and 9,10-dioxa-*anti*-bimanes) which we have developed for efficient discussion of 1,5-diazabicyclo[3.3.0]octadienediones has been thoroughly discussed in ref 1. The use of μ- as an abbreviation for the bridged compounds, for which an extensive description appears in ref 4, is done in analogy with the usage of μ- for bridged inorganic compounds. Formal names can be formulated for example as 4,6-(1,3-tetramethylene)-3,7-dimethyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione for CH_3-μ-C_2.

syn-((CH$_3$OOC)$_2$CHCH$_2$,CH$_3$)B (**7**) (226 mg, 0.5 mmol) in dry DMF (10 mL) was mixed with NaH (60 mg, 1 mM, 60% in oil) at room temperature. After 15 min iodine (274 mg, 1 mmol) was added to the mixture. The solvent was distilled off and the residue chromatographed on silica gel. Elution with dichloromethane/ethylacetate (1:1) afforded μ-((CH$_3$OOC)$_2$C)-*syn*-((CH$_3$OOC)$_2$CHCH,CH$_3$)(CH$_2$,CH$_3$)B (**6**): 35 mg (14%); yellow oil; IR (neat) 3000–2800, 1270, 1630, 1460, 1440, 1380, 1260, 1100, 1030, 860, 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.8 (s, 3 H), 1.86 (s, 3 H), 3.35 (br s, 2 H), 3.58 (s, 3 H), 3.62 (s, 3 H), 3.7 (s, 6 H), 4.0 (d, 1 H, J = 9 Hz), 4.6 (d, 1 H, J = 9 Hz) ppm; UV (CH$_3$CN) λ_{max} 335 nm (ϵ 4500), 250 sh (6100), 232 (15 370); fluorescence maxima (CH$_3$CN) 443 nm, 460 sh (Φ_F 0.2); mass spectrum m/e 450 (M$^+$).

Method B. To a 250-mL three-necked flask equipped with two graphite rod electrodes, were added *syn*-((CH$_3$OOC)$_2$CHCH$_2$,CH$_3$)B (452 mg, 1 mmol) and NaI (6.5 g, 0.04 mol) in 130 mL methanol. The mixture was heated to 60 °C, the heat source removed and the solution electrolyzed; by using with a constant current of 400 mA at 11 V for 10 min with gentle magnetic stirring. The methanol was then evaporated and the residue chromatographed as described in method A, affording 120 mg (30% yield) of product (**6**).

Tetramethyl 1,1,2,2-Ethanetetracarboxylate. Tetraethyl 1,1,2,2-ethanetetracarboxylate was prepared by oxidative coupling of dimethyl malonate with iodine in 30% yield:[37,38] mp 130 °C; ^{1}H NMR (CDCl$_3$) 3.8 (s, 1 H), 4.2 (s, 6 H) ppm; mass spectrum m/e 262 (M$^+$).

μ-((CH$_3$OOC)$_2$CC(COOCH$_3$)$_2$)-*syn*-(CH$_2$,CH$_3$)B (4,6-(1,4-(2,2,3,3-Tetracarbomethoxytetramethylene)-3,7-dimethyl-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-dione) (4). Tetramethyl 1,1,2,2-ethanetetracarboxylate (262 mg, 1 mmol) in 5 mL dry DMSO was added over 5 min to hot sodium methoxide, prepared from sodium (46 mg, 2 mg at.) and 5 mL of dry methanol, removal of the methanol, and dissolution in 4 mL of the white powder in dry DMSO. A solution of *syn*-(CH$_2$Br,CH$_3$)B (**5**) (400 mg, 1.2 mmol) in 5 mL dry DMSO was added dropwise over 5 min at 10 °C under nitrogen. The solution was left standing overnight at room temperature. The solvent was removed under vacuum, the residue dissolved in chloroform, and the solution filtered. The chloroform was evaporated and the residue chromatographed on silica gel. Elution with dichloromethane/ethyl acetate (1:1) afforded μ-((CH$_3$OOC)$_2$CC-(COOCH$_3$)$_2$)-*syn*-(CH$_2$,CH$_3$)B (**4**): 60 mg (11% yield); yellow twinned crystals from methanol; mp 205 °C; IR (KBr) 3020–2850, 1745, 1735, 1730, 1630, 1440, 1430, 1410, 1300, 1280, 1250, 1220, 1140, 1080, 1035, 1020, 930, 920, 840, 790, 750, 700 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.80 (s, 3 H), 3.50 (s, 2 H), 3.75 (s, 6 H) ppm; UV (CH$_3$CN) λ_{max} 355 nm (ϵ 5480), 250 sh (5120), 235 (19 000); fluorescence maxima (CH$_3$CN) 440 nm, 455 nm (sh) (Φ_F 0.73); mass spectrum m/e 450 (M$^+$).

General Procedure for 3-Keto Esters. (The quantities of solvent are given for syntheses using 0.1 mol of acyl chloride.) The 3-keto ester synthesis via 2,2-dimethyl-1,3-dioxan-4,6-dione (Meldrum's acid) is described under bis-pyrazolinones (Method B, see below), since the ester was neither isolated nor characterized.

In a three-necked flask equipped with a dropping funnel and a reflux condenser were placed magnesium (2.1 equivs), dry THF (120 mL), and a crystal of iodine. The reaction was carried out under nitrogen. A solution of isopropyl bromide (2 equivs) in THF (120 mL) was added over 1 h, and the stirring continued for 45 min. The solution was then diluted with THF (800 mL) and dry potassium methyl malonate for **8a–d**, or potassium ethyl methylmalonate for **8e–g** (2 equivs) was added over 20 min via a solids funnel. The reaction is exothermic with evolution of propane. The slurry was refluxed for 2 h (after 20–30 min, evolution of propane ceased) and then cooled to room temperature. A solution of acyl chloride (1 equiv) in THF (40 mL) was added dropwise over 10 min and stirring continued for 15 h. The reaction mixture was then poured, with vigorous stirring, into 95–97% sulfuric acid (28 mL) diluted with ice water (300 mL). The organic layer was separated, the aqueous phase extracted with ether (3 × 100 mL), and the extract combined with the organic layer. The solvent was removed, dichloromethane (600 mL) added, and the organic layer separated, washed with saturated aqueous NaHCO$_3$ (400 mL) and with saturated aqueous NaCl (100 mL), dried over MgSO$_4$, and filtered. Evaporation of the solvent afforded the corresponding bis-3-keto esters **8a–g** which were used without further purification.

Succinyl chloride (34.5 g, 0.15 mol) and potassium methyl malonate gave dimethyl 3,6-dioxooctanedioate (**8a**)[41] as an oil: 32.2 g (93% yield); ^{1}H NMR (CDCl$_3$) 2.92 (4 H, s), 3.60 (4 H, s), 3.76 (6 H, s) ppm. Glutaryl chloride (0.05 mol) and potassium methyl malonate gave dimethyl 3,7-dioxononanedioate (**8b**) as a yellow oil: 8.55 g (70% yield); ^{1}H NMR (CDCl$_3$) 1.87 (t, 2 H, J = 7 Hz), 2.614 (t, 4 H, J = 7 Hz), 3.454 (s, 4 H), 3.73 (s, 6 H) ppm. Adipoyl chloride (0.05 mol) and potassium ethyl malonate yielded diethyl 3,8-dioxodecanedioate (**8c**) as an oil: 12 g (85% yield); bp 176–179 °C (0.01 torr); ^{1}H NMR (CDCl$_3$) 1.22 (t, 6 H), 1.58 (m, 4 H), 2.52 (m, 4 H), 3.37 (s, 4 H), 4.23 (q, 4 H), 4.93 (s, 1 H, enol) ppm.[57] Pimeloyl chloride (0.05 mol) and potassium methyl malonate yielded dimethyl 3,9-dioxoundecanedioate (**8d**) as a yellow oil: 11.3 g (83% yield); ^{1}H NMR (CDCl$_3$) 1.2–2.0 (m, 6 H), 2.4–2.8 (m, 4 H), 3.41 (s, 4 H), 3.69 (s, 6 H) ppm. Succinyl chloride (0.055 mol) and potassium ethyl methylmalonate (**8e**) gave diethyl 2,7-dimethyl-3,6-dioxooctanedioate as a yellow oil: 15.1 g (97% yield); ^{1}H NMR (CDCl$_3$) 1.276 (t, J = 7 Hz, 3 H), 1.351 (d, J = 7.1 Hz, 3 H), 2.856 (s, 2 H), 3.586 (q, J = 7 Hz, 2 H), 4.197 (q, J = 7 Hz, 1 H) ppm. Glutaryl chloride (0.086 mol) and potassium ethyl methylmalonate (0.24 mol) yielded diethyl 2,8-dimethyl-3,7-dioxononanedioate (**8f**) as a yellow oil: 20.53 g (79.4% yield); ^{1}H NMR (CDCl$_3$) 1.25 (t, 6 H, J = 7 Hz), 1.40 (d, 6 H, J = 6 Hz), 1.85 (t, 2 H, J = 7 Hz), 2.575 (t, 4 H, J = 4.5 Hz), 3.475 (q, 2 H, J = 6 Hz), 4.10 (q, 4 H, J = 7 Hz) ppm. Adipoyl chloride (0.05 mol) and potassium ethyl methylmalonate yielded diethyl 2,9-dimethyl-3,8-dioxodecanedioate (**8g**) as a yellow oil: 24 g (76% yield); ^{1}H NMR (CDCl$_3$) 1.25 (t, J = 11.7 Hz, 3 H), 1.50 and 1.60 (2 singlets, 3 H), 1.94 (m, 1 H), 2.50 (m, 4 H), 3.50 (q, J = 11.7 Hz, 1 H), 4.13 (q, J = 11.7 Hz, 2 H) ppm; IR (CHCl$_3$) 1745, 1720 cm^{-1}; mass spectrum m/e 314 (15) (M$^+$).

General Procedure for Bis-pyrazolinones. The bis-3-keto ester (**8a–g**) was added over 1 h to a solution of hydrazine (1.1 equiv) in ethanol or methanol (100 mL for 0.04 mol) and the mixture refluxed for 1–3 h and then stirred overnight at room temperature. The precipitated bis-pyrazolinone was filtered off and used without further purification (method A). In method B, the bis-3-keto ester was generated from Meldrum's acid and reacted with hydrazine in a "one-pot" synthesis.

Dimethyl 3,6-dioxooctanedioate (36.2 g, 0.16 mol) and hydrazine in methanol gave 3,3′-dimethylenebis(pyrazol-2-in-5-one) (**9a**) as a solid insoluble in all common solvents, 21.2 g (72% yield). Dimethyl 3,7-dioxononanedioate (**8b**) (0.035 mol) and hydrazine in methanol yielded 3,3′-trimethylenebis(pyrazol-2-in-5-one) (**9b**) as a pale yellowish powder: 5.45 g (74.8% yield); mp 280 °C; IR (KBr) 3000–2500, 1680, 1610, 1550, 1515, 1475, 1405, 1170, 1140, 1040, 1010, 960, 925, 765 cm^{-1}; ^{1}H NMR (DMSO-d_6) 1.79 (m, 2 H), 2.48 (m, 4 H), 5.25 (s, 4 H), 10.45 (m, 2 H) ppm. Diethyl 3,8-dioxodecanedioate (**8c**) (12 g, 0.042 mol) and hydrazine in ethanol yielded 3,3′-tetramethylenebis(pyrazol-2-in-5-one) (**9c**) as a yellowish powder: 5.6 g (60% yield); mp 275 °C dec; IR (KBr) 2570–2000 (br), 1615, 1550, 1510, 1260, 1230, 1180, 1010, 980 cm^{-1}; ^{1}H NMR (DMSO-d_6) 1.40 (m, 2 H), 2.25 (m, 2 H), 3.0 (s, 1 H) ppm; UV (CH$_3$OH) λ_{max} 243 nm (ϵ 2400), 217 (920); mass spectrum m/e 222 (32) (M$^+$).

Method B. To a dichloromethane solution of Meldrum's acid (18 g, 012 mol) and pyridine (1.90 mL, 0.024 mol) was added adipoyl chloride (12 g, 0.0066 mol) dropwise at 0 °C over 0.5 h and stirred at 0 °C for 1 h and then at room temperature for 1 h, all under nitrogen. After the Meldrum's acid had disappeared (TLC, ethyl acetate, silica plates) 6 N HCl (5 mL) was added at 0 °C, and the dichloromethane layer separated, dried over MgSO$_4$, and evaporated to give, after washing with acetone to remove unreacted Meldrum's acid, 1,6-hexanedioyl-5,5′-bis-(2,2-dimethyl1-1,3-dioxane-4,6-dione), **14** g (ca. 45% yield), as a white solid: mp 110 °C dec; IR (KBr) 3420, 2960, 1735, 1660, 1550, 1405, 1360, 1300, 1270, 1210, 1160, 1040, 1025, 930, 810, 790, 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) 1.68 (s, 6 H), 1.75 (t, J = 6 Hz, 2 H), 3.00 (t, J = 6 Hz, 2 H), 15.0 (br s, 1 H) ppm; UV (CH$_3$CN) λ_{max} 263 nm (ϵ 22 940); mass spectrum m/e 368 (M$^+$ 398 − 30).

1,6-Hexanedioyl-5,5′-bis(2,2-dimethyl-1,3-dioxane-4,6-dione) (30 g, 0.075 mol) was added to absolute ethanol (200 cm^3) and refluxed for 1–2 h. Half of the ethanol was distilled off to ensure removal of acetone. The bis-3-keto ester **8c** was not isolated. Hydrazine (5.2 cm^3, 0.16 mol) was added all at once to the solution of bis-3-keto ester **8c** and the solution refluxed for 1 h. The bis-pyrazolinone **9c** precipitated as a yellowish powder, 15 g (89.6% yield).

Dimethyl 3,9-dioxoundecanedioate (**8d**) (11.3 g, 0.042 mol) and hydrazine in methanol gave 3,3′-pentamethylenebis(pyrazol-2-in-5-one) (**9d**) as a white solid: 3.124 g (32% yield); mp > 280 °C; IR (KBr) 3000–2500, 1620, 1500, 1190, 1015, 985, 835, 760, 650 cm^{-1}. Diethyl 2,7-dimethyl-3,6-dioxooctanedioate (15.1 g, 0.053 mol) and hydrazine in ethanol yielded 3,3′-dimethylenebis(4-methylpyrazol-2-in-5-one) (**9e**) as a white solid, 10.8 g (92% yield). Diethyl 2,8-dimethyl-3,7-dioxononanedioate (**8f**) (20.53 g, 0.068 mol) and hydrazine in ethanol gave 3,3′-trimethylenebis(4-methylpyrazol-2-in-5-one) (**9f**) as a white solid: 11.07 g (68.4% yield); mp > 280 °C; IR (KBr) 3000–2500, 1605, 1210, 925, 785, 720 cm^{-1}; ^{1}H NMR (DMSO-d_6) 1.73 (s, 6 H), 1.79 (m, 2 H), 2.42 (t, J = 7.5 Hz, 4 H) ppm. Diethyl 2,9-dimethyl-3,8-dioxodecanedioate (**8g**) (24.2 g, 0.076 mol) and hydrazine in ethanol gave 3,3′-tetramethylenebis(4-methylpyrazol-2-in-5-one) (**9g**) as a white powder: 11.4 g (60% yield), mp 310 °C dec; ^{1}H NMR (DMSO-d_6) 1.479 (m, 2 H), 1.723 (s, 3 H), 2.410 (m, 2 H) ppm; mass spectrum m/e 250 (M$^+$).

General Procedure for Di- and Tetrachloropyrazolinones. Chlorine was bubbled into a suspension of bis-pyrazolinone **9a–g** in dichloromethane.

After the chlorination was completed (the yellow-green color of chlorine persists), air was passed through the solution to remove chlorine and hydrogen chloride. If the product is soluble, 2-methyl-2-propanol (1 mol/mol HCl) may be added to consume hydrogen chloride, the water formed being removed with $MgSO_4$. The solvent is evaporated and the product purified by "flash" chromatography on silica gel, if necessary. If the product is insoluble, no additions are made and isolation is accomplished by simple filtration.

The bis-pyrazolinone (**9a**) (9.7 g, 0.05 mol) was chlorinated in dichloromethane (200 mL). After reaction, filtration yielded 3,3′-dimethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10a**) that was recrystallized from acetonitrile, 14.3 g (86% yield), mp 170 °C dec. The bis-pyrazolinone (**9b**) (5.205 g, 0.025 mol) was reacted with chlorine in CH_2Cl_2 (150 mL). Flash chromatography with dichloromethane/ethyl acetate (9:1) as eluant yielded 3,3′-trimethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10b**), 4.325 g (50% yield). The bis-pyrazolinone (**9c**) (18 g, 0.081 mol) was reacted with chlorine in CH_2Cl_2 (250 mL). Evaporation of the solvent and recrystallization from acetonitrile yielded 3,3′-tetramethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10c**) as a white solid: 22 g (75% yield), mp 160 °C; IR (KBr) 3250, 1750, 1730, 1420, 1380, 1290, 1250, 1200, 1160, 1060, 1010, 910, 850, 800, 740 cm^{-1}; ^1H NMR ($CDCl_3$) 1.776 (m, 1 H), 2.0308 (m, 2 H), 2.9820 (br s, 2 H) ppm; UV (CH_3CN) λ_{max} 282 (ϵ 5100), 275 sh (5000); mass spectrum *m/e* 323, 325 ($M^+ - Cl$) (corresponds to pattern expected for a compound containing 3 Cl with no signal at *m/e* 360).[56] The bis-pyrazolinone (**9d**) (1.772 g, 0.0075 mol) was reacted with chlorine in dichloromethane (50 mL). After evaporation of the solvent the residue was purified by flash chromatography with dichloromethane/ethyl acetate (1:1) as eluant to yield 3,3′-pentamethylenebis(4,4-dichloropyrazol-2-in-5-one) (**10d**), 2.008 g (71.6% yield), as a heavy, slightly yellow oil: ^1H NMR ($CDCl_3$) 1.522–1.606 (m, 2 H), 1.834 (quint, J = 7.5 Hz, 4 H), 2.636 (t, J = 7.5 Hz, 4 H), 9.695 (br s, 2 H) ppm. The bis-pyrazolinone (**9e**) (2.22 g, 0.01 mol) was reacted with chlorine in dichloromethane (100 mL). Filtration yielded 3,3′-dimethylenebis(4-chloro-4-methylpyrazol-2-in-5-one) (**10e**) as a white solid: 2.88 g (99% yield); ^1H NMR (CH_3CN-d_3) 1.66 (s, 3 H). The bis-pyrazolinone (**9f**) (3.54 g, 0.015 mol) was reacted with chlorine in dichloromethane (90 mL). After removal of solvent, the residue was purified by flash chromatography with dichloromethane/ethylacetate (1:1) as eluant to yield 3,3′-trimethylenebis(4-chloro-4-methylpyrazol-2-in-5-one) (**10f**), 3.57 g (78% yield), as a white solid: mp 134 °C; IR (KBr) 3250, 3110, 2990, 2920, 1730, 1615, 1555, 1430, 1390, 1320, 1260, 1220, 1160, 1115, 1075, 1060, 860 cm^{-1}; ^1H NMR ($CDCl_3$) 1.705 (s, 3 H), 2.190 (q, J = 7.3 Hz, 1 H), 2.475–2.703 (m, 2 H), 8.992 (s, 1 H), 9.015 (s, 1 H) ppm; mass spectrum *m/e* 270, 268 ($M^+ - Cl$).[56] The bis-pyrazolinone (**9g**) (11 g, 0.044 mol) was reacted with chlorine in dichloroethane (500 mL). The product, 3,3′-tetramethylenebis(4-chloro-4-methylpyrazol-2-in-5-one) (**10g**), precipitated as a fine white powder: 14 g (100% yield); mp 197 °C dec; ^1H NMR (DMSO-d_6) 1.68 (m, 2 H), 1.56 (s, 3 H), 2.45 (m, 2 H) ppm; mass spectrum, 283 ($M^+ - Cl$), 248 ($M^+ - 2Cl$) fits 2Cl (no peak at *m/e* 320).[56]

General Procedure for Tricyclic Bimanes. Diisopropyl ethylamine (1 equiv) was added to a solution or suspension of di- or tetrachloropyrazolinone (**10b–d,f,g**) in dichloromethane. The reaction mixture was protected from light and the reaction followed by TLC. In the case of **10b–d**, the mixture was maintained at 0 °C for about 1 h and then at room temperature for 1 h. In the case of **10f** and **10g**, the reaction mixture was stirred overnight at room temperature. After reaction was complete, the solvent was evaporated and the residue flash chromatographed on silica gel. All of the products were fluorescent solids.

Cl-μ-C_1 (4,6-(1,3-Trimethylene)-3,7-dichloro-1,5-diazabicyclo[3.3.0]-octa-3,6-diene-2,8-dione) (3b). The reaction of 3.46 g (0.01 mol) of **10b** gave 1.523 g (0.0062 mol) of **3b** (62% yield), when eluted with dichloromethane/ethyl acetate (19:1): yellow crystals from $CHCl_3$; mp 235–237 °C; IR (KBr) 1775, 1760, 1705, 1620, 1605, 1475, 1390, 1320, 1220, 1190, 1120, 965, 750 cm^{-1}; ^1H NMR ($CDCl_3$) 2.260 (q, J = 6 Hz, 2 H), 2.909 (t, J = 6 Hz, 4 H) ppm; ^{13}C NMR ($CDCl_3$) 21.55 ($CH_2C\underline{H}_2CH_2$), 23.25 ($CH_2\underline{C}H_2CH_2$), 107.66 (CO—*C*=), 151.84 (=*C*—N), 156.93 (C=O) ppm; UV (CH_3CN) λ_{max} 347 nm (ϵ 5700), 235 (15 880); fluorescence maxima (CH_3CN) 444 nm, 462 sh, 480 sh (Φ_F 0.85); fluorescence maxima (solid) λ_{max} 465 nm, 480 sh; fluorescence excitation maxima (solid) 330 nm, 360 sh, 380, 400, 410 sh, 420 sh; mass spectrum *m/e* 248, 246, 244 (M^+) (fits 2Cl with *m/e* 244 = 100).[56]

Cl-μ-C_2 (4,6-(1,4-Tetramethylene)-3,7-dichloro-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-dione) (3c). The reaction of 4.34 g (0.012 mol) of **10c** gave 2.74 g (0.0108 mol) of **3c** (88% yield), when eluted with dichloromethane/ethyl acetate (19:1): yellow needles, mp 247 °C (dec pt 217 °C); IR (KBr) 3210, 2960, 1770, 1760, 1730, 1600, 1460, 1430, 1380, 1340, 1280, 1160, 1080, 1010, 910, 850 cm^{-1}; ^1H NMR ($CDCl_3$) 2.0248 (q, 2 H), 2.9814 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) 23.830 ($CH_2\underline{C}H_2CH_2$), 26.885 ($\underline{C}H_2$—C=C), 108.220 (C=*C*—Cl), 151.518 (*C*=C—Cl), 155.428 (C=O) ppm; UV (CH_3CN) λ_{max} 374 nm (ϵ 6000), 250 sh (8460), 234 (13 230); fluorescence maxima (CH_3CN) 444 nm, 460 sh (Φ_F 0.86); fluorescence maxima (solid) 465 nm, 480 sh; fluorescence excitation maxima (solid) 330 nm, 360 sh, 380, 400, 410 sh, 425 sh; mass spectrum *m/e* 258, 260, 262 (M^+) (fits 2Cl with *m/e* 258 = 100).[56]

Cl-μ-C_3 (4,6-(1,5-Pentamethylene)-3,7-dichloro-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-dione) (3d). The reaction of 371 mg (0.991 mmol) of **10d** gave 64 mg (0.232 mmol) of **3d** (23.4% yield), when eluted with dichloromethane and then dichloromethane/ethyl acetate (9:1): yellow crystals; mp 225 °C; IR (KBr) 3000–2800, 1765, 1695, 1605, 1460, 1360, 1280, 1260, 1180, 800, 730 cm^{-1}; ^1H NMR ($CDCl_3$) 1.512 (q, J = 3 Hz, 2 H), 1.928 (q, J = 6 Hz, 4 H), 3.011 (t, J = 7 Hz, 4 H) ppm; ^{13}C NMR ($CDCl_3$) 23.62 ($CH_2CH_2\underline{C}H_2CH_2CH_2$), 23.89 ($CH_2\underline{C}$-$H_2CH_2CH_2CH_2$), 24.67 (C=C—$\underline{C}H_2$), 109 (CCl), 149.59 (*C*=C—Cl), 155.36 (C=O) ppm; UV (CH_3CN) λ_{max} 375 nm (ϵ 7430), 250 sh (10 000), 234 (19 050); fluorescence maxima (CH_3CN) 440 nm, 460 sh (Φ_F 0.4); fluorescence maxima (solid) 465 nm, 480 sh; fluorescence excitation maxima (solid) 340 sh, 360 sh, 380, 400, 410, 420, 440; mass spectrum *m/e* 276 (9), 275 (8), 274 (63), 273 (13), 272 (100) (M^+) (fits 2Cl with *m/e* 276).[56]

CH_3-μ-C_1 (4,6-(1,3-Trimethylene)-3,7-dimethyl-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-dione) (3f). The reaction of 1.83 g (6 mmol) of **10f** gave 392 mg (1.92 mmol) of **3f** (32% yield), when eluted with ethyl acetate/dichloromethane (1:1): fluffy white needles; mp 239–240 °C; IR (KBr) 2970, 2930, 1745, 1690, 1630, 1460, 1440, 1415, 1390, 1350, 1260, 1175, 1150, 1105, 1015, 870, 780, 755, 730 cm^{-1}; ^1H NMR ($CDCl_3$) 1.799 (s, 3 H), 2.119 (quint, J = 6 Hz, 1 H), 2.752 (t, J = 6 Hz, 2 H) ppm; ^{13}C NMR ($CDCl_3$) 6.43 (CH_3), 21.69 ($CH_2\underline{C}H_2CH_2$), 24.46 ($CH_2\underline{C}H_2CH_2$), 110.68 (*C*—CH_3), 152.47 (=C—N), 162.94 (C=O) ppm; UV (CH_3CN) λ_{max} 334 nm (ϵ 4900), 229 (16 500); fluorescence maxima (CH_3CN) 439 nm, 460 sh (Φ_F 0.87); fluorescence maxima (solid state) λ_{max} 440 nm, 460 sh; fluorescence excitation maxima (solid state) 340 sh, 360 sh, 380, 400, 410 sh; mass spectrum *m/e* 204 (M^+, 100).

CH_3-μ-C_2 (4,6-(1,4-Tetramethylene)-3,7-dimethyl-1,5-diazabicyclo-[3.3.0]octa-3,6-diene-2,8-dione) (3g). The reaction of 7 g (0.022 mol) of **10g** gave 4.6 g (0.021 mol) of **3g** (96% yield), when eluted with ethyl acetate/dichloromethane (3:7): yellow solid; mp 235 °C (EtAc); IR (KBr) 2920, 1745, 1670, 1620, 1600, 1540, 1455, 1420, 1350, 1240, 1120, 1100, 800, 740 cm^{-1}; IR ($CHCl_3$) 1746.0, 1666.7, 1623.6, 1602.1, 1540.5, 1455.3, 1417.2, 1407.4, 1385.8 cm^{-1}; ^1H NMR ($CDCl_3$) 1.8279 (s, 3 H), 1.9671 (quint, J = 0.7 Hz, 2 H), 2.8329 (m, 2 H) ppm; ^{13}C NMR ($CDCl_3$) 6.99 (CH_3), 24.46 ($\underline{C}H_2CH_2$—C=), 26.42 ($\underline{C}H_2$—C=), 111.38 (C=*C*—CH_3), 151.17 (C=*C*—CH_3), 161.40 (C=O) ppm; UV (CH_3CN) λ_{max} 366 nm (ϵ 5800), 262 sh (6260), 230 (15 980); fluorescence maxima (CH_3CN) 440 nm, 460 sh (Φ_F 0.68); fluorescence maxima (solid) λ_{max} 465 nm, 480 sh; fluorescence excitation maxima (solid) 340 sh, 360 sh, 380 sh, 400, 410, 420, 440 sh; mass spectrum *m/e* 218 (M^+).

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Supplementary Material Available: Tables of atomic positional and equivalent isotropic parameters for **3b**, **3c**, and **3d**, dihedral angles and absorption maxima for bimanes, bond lengths, thermal vibration amplitudes, and geometric parameters (8 pages). Ordering information is given on any current masthead page.