Heteroatom Chemistry
Volume 1, Number 3, 1990

Bimanes (1,5-Diazabicyclo[3.3.0]octadienediones): Laser Activity in *syn*-Bimanes

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Received 6 October 1989.

ABSTRACT

The conversion of 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one **10b** *was catalyzed by a mixture of potassium fluoride and alumina to give* syn-(*methyl,benzyl)bimane* **6** *(62%) without detectable formation of the* anti *isomer* **A6** *[a 1 : 1 mixture (87%) of the isomers* **6** *and* **A6** *was obtained when the catalyst was potassium carbonate]. In a similar reaction* syn-(*methyl,carboethoxymethyl)bimane* **7** *(15%) with the* anti *isomer* **A7** *(36%) was obtained from 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one* **10c**. syn-(*Methyl,β-acetoxyethyl)bimane* **8** *(70%) was obtained from 3-methyl-4-β-acetoxyethyl-4-chloro-2-pyrazolin-5-one* **10d** *(potassium carbonate catalysis) and was converted by hydrolysis to* syn-(*methyl,β-hydroxyethyl)bimane* **9** *(40%). Acetyl nitrate (nitric acid in acetic anhydride) converted* anti-(*amino,hydrogen)bimane* **11** *to* anti-(*amino,nitro)bimane* **15** *(91%),* anti-(*methyl,hydrogen)bimane* **13** *to* anti-(*methyl,nitro)(methyl,hydrogen)bimane* **16** *(57%), and degraded* syn-(*methyl,hydrogen)bimane* **12** *to an intractable mixture. Treatment with trimethyl phosphite converted* syn-(*bromomethyl,methyl)bimane* **17** *to* syn-(*dimethoxyphosphinylmethyl,methyl)bimane* **18** *(78%) that was further converted to* syn-(*styryl,methyl)bimane* **19** *(29%) in a condensation reaction with benzaldehyde. Treatment with acryloyl chloride converted* syn-(*hydroxymethyl,methyl)bimane* **20** *to its acrylate ester* **21** *(22%). Stoichiometric bromination of* syn-(*methyl,methyl)bimane* **1** *gave a monobromo derivative that was converted* in situ *by treatment with potassium acetate to* syn-(*acetoxymethyl,methyl)(methyl,methyl)bimane* **47**. *N-Amino-μ-amino*-syn-(*methylene,methyl)bimane* **24** *(68%) was obtained from a reaction between the dibromide* **17** *and hydrazine. Derivatives of the hydrazine* **24** *included a perchlorate salt and a hydrazone* **25** *derived from acetone. Dehydrogenation of* syn-(*tetramethylene)bimane* **26** *by treatment with dichlorodicyanobenzoquinone (DDQ) gave* syn-(*benzo,tetramethylene)bimane* **27** *(58%) and* syn-(*benzo)bimane* **28** *(29%). Bromination of the bimane* **26** *gave a dibromide* **29** *(92%) that was also converted by treatment with DDQ to* syn-(*benzo)bimane* **28**. *Treatment with palladium (10%) on charcoal dehydrogenated 5,6,10,11-tetrahydro-7*H,*9*H-*benz[6,7]indazol[1,2-*a]*benz*[g]*indazol-7,9-dione* **35** *to* syn-(*α-naphtho)bimane* **36** *(71%). The bimane* **35** *was prepared from 1,2,3,4-tetrahydro-1-oxo-2-naphthoate* **37** *by stepwise*

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*treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H-*benz*[g]*indazol-3-one* ***38****, followed by chlorine to give 3a-chloro-2,3a,4,5-tetrahydro-3*H-*benz*[g]*indazol-3-one* ***39****, and base. Dehydrogenation over palladium converted the indazolone* ***34*** *to 1*H-*benz*[g] *indazol-3-ol* ***36****. Helicity for the hexacyclic* syn-(*α-naphtho)bimane* ***36*** *was confirmed by an analysis based on molecular modeling.*

The relative efficiencies (RE) for laser activity in the spectral region 500–530 nm were obtained for 37 syn-*bimanes by reference to coumarin 30 (RE 100): RE > 80 for* syn-*bimanes* ***3****,* ***5****,* ***18****, and μ-(dicarbomethoxy)methylene*-syn-(*methylene,methyl)bimane* ***22****: RE 20–80: for* syn-*bimanes* ***1****,* ***2****,* ***4****,* ***20****,* ***24****,* ***26****, and μ-thia*-syn-(*methylene,methyl)bimane* ***50****: and RE 0-20 for 26* syn-*bimanes. The bimane dyes tended to be more photostable and more water-soluble than coumarin 30. The diphosphonate* ***18*** *in dioxane showed laser activity at 438 nm and in water at 514 nm. Presumably helicity, that was demonstrated by molecular modeling, brought about a low fluorescence intensity for* syn-(*α-naphtho)bimane* ***36****, Φ0.1, considerably lower than obtained for* syn-(*benzo)bimane* ***28****, Φ0.9.*

INTRODUCTION

Following its discovery in 1966 the dye laser [1] depended on the availability of laser dyes to provide coherent light over the spectral region from ultraviolet (UV) to infrared (IR). This laser activity was obtained from cyanine, xanthene (including rhodamine and fluoroscein), triarylmethane, acridine, azine, and chlorophyll dyes; linear and condensed polybenzenoid molecules; and certain heterocycles that included coumarins, quinolones, oxazoles, pyrazolines, and furans. In 1984, over 600 laser dyes were listed [2].

Parameters for a laser dye included high quantum fluorescence yield, (generally $\Phi > 0.7$), minimal overlap of fluorescence with onset of absorption (S-S) and triplet-triplet (T-T) spectral regions, photostability, efficiency in power output, favorable solubility and interaction with the solvent, and availability [3]. Other factors also contributed to the laser performance. Aqueous solutions of a dye (10^{-4} molar was generally desirable) offered the superior thermo-optic properties of water that often improved laser activity [5c]. Groups that enhanced intersystem crossing ($S_1 \rightarrow T_1$) through the heavy atom effect could interfere with laser activity and were generally avoided [3]. It was sometimes assumed that somewhat less than expected laser power output was the result of (1) nonradiative transfer ($S_1 \rightarrow S_0$), (2) loss of electronic excitation through reversible charge transfer with the chromophore, and/or (3) self-quenching through dye aggregation [3]. About 125 tunable laser dyes more or less satisfied these special conditions and became commercially available to cover the region from 300–1200 nm [4].

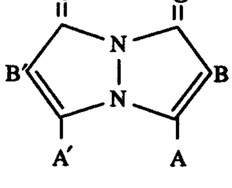
Other investigations led us to examine *syn*-bimanes (1,5-diazabicyclo[3.3.0]octadiene-2,8-diones) as laser dyes. Kosower introduced a system of trivial nomenclature for the bimanes based on substitution types. Type I: *syn*-(A,B)bimanes, Type II: *syn*-(A,B)(A′,B′)bimanes, Type III: μ-X-*syn*-(methylene,methyl)bimanes, Type IV: *anti*-(A,B)bimanes, and Type V: *anti*-(A,B)(A′,B′)bimanes were adopted for this report [6, 7].

Laser activity in the spectral region 500–530 nm from *syn*-(methyl,methyl)bimane **1** was reported in 1986 [5a]. The discovery of similar activity from *syn*-(methyl,chloro)bimane **2**, *syn*-(acetoxymethyl,methyl)bimane **3**, *syn*-(fluoromethyl,methyl)bimane **4**, and μ-(dicarboethoxy) methylene-*syn*-(methylene,methyl)bimane **5** followed rapidly [5b–d]. In our ongoing search for laser dyes it became desirable to examine greater diversification in substitution patterns in *syn*-bimanes.

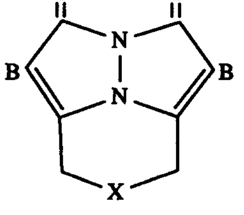
syn-*BIMANE DYE PREPARATIONS AND PROPERTIES*

Background Information

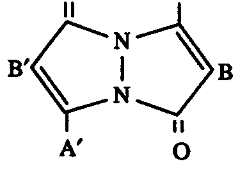
Variation in substitution patterns in *syn*-bimanes has remained limited. In the Kosower scheme for their synthesis chlorination of a pyrazolinone followed by treatment with a base (potassium carbonate or a tertiary amine) brought about the forma-



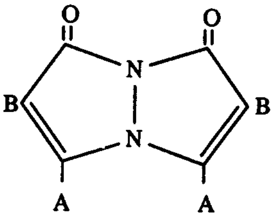
Type I: A,B = A′,B′
Type II: A,B ≠ A′,B′



Type III: X = C,N,S



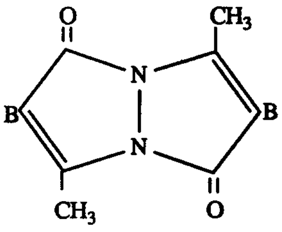
Type IV: A,B = A′,B′
Type V: A,B ≠ A′,B′



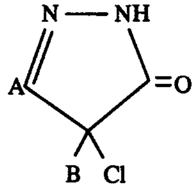
Compound	*A*	*B*	*Cpd*	*A*	*B*
1	CH_3	CH_3	**12**	CH_3	H
2	CH_3	Cl	**17**	$BrCH_2$	CH_3
3	$CH_3CO_2CH_2$	CH_3	**18**	$(CH_3O)_2P(O)CH_2$	CH_3
4	FCH_2	CH_3	**19**	$C_6H_5CH{=}CH$	CH_3
6	CH_3	$CH_2C_6H_5$	**20**	$HOCH_2$	CH_3
7	CH_3	$CH_2CO_2C_2H_5$	**21**	$CH_2{=}CHOCOCH_2$	CH_3
8	CH_3	$CH_2CH_2O_2CCH_3$	**43**	CH_3	C_6H_5
9	CH_3	CH_2CH_2OH	**44**	C_6H_5	Cl
			45	C_2H_5OCO	Cl

tion of mixtures of *syn*- and *anti*-bimanes, eq. (1) [6–8]. Selected conversions afforded preparative amounts of *syn*-bimanes with a limited range of substituents. *syn*-Bimanes with strong electron donating or withdrawing substituents were not prepared by this method and remain largely unknown. The chemical reactivity needed for further conversion of a substituent, e.g., methyl to acetoxymethyl [8] was restricted to the short axis where substituents ran parallel with the NN bond.

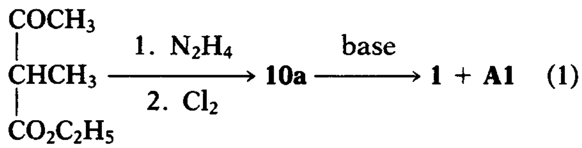
Chemical reactivity, "normal" positions of nuclear magnetic resonance (NMR) signals, and the occurrence of planar and nonplanar molecules in the crystal were properties that supported the perception of *syn*- and *anti*-bimanes as examples of α,β-unsaturated amide systems with no implication of "aromatic character" [6]. The fluorescence, $\Phi > 0.7$, from many *syn*-bimanes was, nevertheless, assumed to be a property of aromaticity insofar as strong fluorescence from an organic compound that was not aromatic has remained virtually unknown [5b]. A weak fluorescence from *anti*-bimanes [6] was shared with other pyrazolinones [9], γ-pyridones [10], maleimides [11], and presumably other quasiaromatic cyclic amides and hydrazides. A strong phosphorescence was noted for *anti*- but not for *syn*-bimanes [6].



A1 B = CH_3
A6 B = $CH_2C_6H_5$
A7 B = $CH_2CO_2C_2H_5$



Compound	*A*	*B*
10a	CH_3	CH_3
10b	CH_3	$CH_2C_6H_5$
10c	CH_3	$CH_2CO_2C_2H_5$
10d	CH_3	$CH_2CH_2O_2CCH_3$
10e	H	$CO_2C_2H_5$

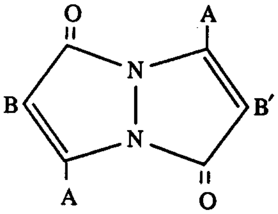


$$\begin{array}{l}COCH_3\\ |\\ CHCH_3\\ |\\ CO_2C_2H_5\end{array} \xrightarrow[2.\ Cl_2]{1.\ N_2H_4} \mathbf{10a} \xrightarrow{\text{base}} \mathbf{1} + \mathbf{A1} \qquad (1)$$

Long Axis (Perpendicular to the NN Bond) Substitution

syn-(Methyl,benzyl)bimane **6** was prepared from 3-methyl-4-benzyl-4-chloro-2-pyrazolin-5-one **10b** (obtained from ethyl benzylacetoacetate by treatment with hydrazine followed by chlorination) under the influence of a novel catalyst [12] that was provided by a mixture of potassium fluoride and alumina. Formation of the *anti*-isomer **A6** was not detected; however, a mixture (1 : 1) of the isomers **6** and **A6** was obtained when potassium carbonate was the catalyst. In related conversions 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one **10c** (from diethyl acetosuccinate) gave *syn*-(methyl,carboethoxymethyl)bimane **7** along with the *anti* isomer **A7**, and 3-methyl-4-β-acetoxyethyl-4-chloro-2-pyrazolin-5-one **10d** (from ethyl β-acetoxyethylacetoacetate) gave *syn*-(methyl,β-acetoxyethyl)bimane **8**. Hydrolysis converted the latter to *syn*-(methyl,β-hydroxyethyl)bimane **9**. Attempts to obtain *syn*-(hydrogen,carboethyoxy)bimane from ethoxymethylenemalonic ester were unsuccessful. Treatment with hydrazine converted the ester to a pyrazolinone that underwent chlorination to a product thought to be the chloropyrazolinone **10e**; however, the latter in the presence of base resisted conversion to a bimane.

To enhance bimane functionality an exploratory investigation of the aromatic nitration of *anti*-(amino,hydrogen)bimane **11** (the *syn* isomer is unknown) and *syn*- and *anti*-(methyl,hydrogen)bimanes **12** and **13** was undertaken. The *anti*-bimane **11** was obtained from N,N'-dicyanoacetohydrazide **14** [$(NHCOCH_2CN)_2$] by cyclization in the presence of sodium bicarbonate [13]. Acetyl nitrate (explosive above 50°C), prepared in situ from a mixture of nitric acid (90%) and acetic anhydride, converted the *anti*-bimane **11** to *anti*-(amino,nitro)bimane **15**, a structure assignment supported by IR, ^{13}C NMR, EI-MS, and elemental analysis. Similar treatment converted *anti*-(methyl,hydrogen)bimane **13** [5] to *anti*-(methyl,nitro)(methyl,hydrogen)bimane **16**. *syn*-(Methyl,hydrogen)bimane **12** [5] was completely converted by similar treatment to an intractable mixture that contained no more than a trace amount of a solid thought to be a mononitro derivative on the basis of M^+ 209 in the EI-MS. These aromatic substitution reactions resembled nitrations of pyrazolinones, hydroxy-, and aminopyrazoles [14] and tended to support quasiaromaticity of the bimane ring systems (see above).



11 A = NH_2, B = B′ = H
13 A = CH_3, B = B′ = H
15 A = NH_2, B = B′ = NO_2
16 A = CH_3, B = NO_2, B′ = H

Attempts to oxidize amino groups in bimanes **11** and **15** to nitro groups were unsuccessful and led instead to intractable mixtures. An unidentified product isolated as a hydrated dipotassium salt $C_6N_4O_8K_2 \cdot 1.5\ H_2O$ from a treatment of diaminodinitrobimane **15** with potassium superoxide represented the oxidation level of a dihydroxydinitrobimane, in which hydroxyl groups had replaced amino groups. A hydrated sodium salt of a dihydroxydinitro-bimane $C_6H_4O_8Na_2 \cdot 1.5\ H_2O$, was previously obtained in an oxidation of the corresponding dioxime [15].

The accessibility of substituted *syn*-bimanes was restricted by degradation of the bimane structure when treated under mild conditions with either an oxidizing reagent or an acid and, as previously reported [6], by ring opening and conversion under alkaline conditions.

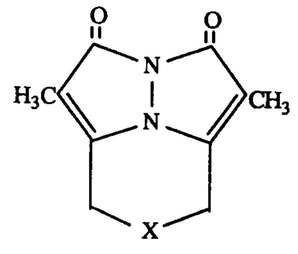
Short Axis (Parallel to the NN Bond) Substitution

Generally substituent variation proceeded from the nonfluorescent *syn*-(bromomethyl,methyl)bimane **17** [obtained from *syn*-(methyl,methyl)bimane **1** by bromination [7]. Conversion of the dibromide **17** to *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18** was brought about by treatment with trimethylphosphite. A need for polymerizable *syn*-bimane monomers to be formulated into glassy polymer slugs led to the preparation of *syn*-(styryl,methyl) bimane **19** (from the diphosphonate **18** and benzaldehyde) and the acrylate ester **21** of *syn*-(hydroxymethyl,methyl)bimane **20** (from the dibromide **17** by treatment with alkali followed by esterification of the glycol **20** with acryloyl chloride). Laser activity from dyes in polymeric glasses [16] will be described elsewhere.

Stoichiometry controlled a monobromination of the bimane **1** [6, 8]. Without isolation the bromide was treated with potassium acetate to give *syn*-(acetoxymethyl,methyl)(methyl,methyl) bimane **47**.

μ-Bridged syn-*Bimanes*

Ring closure between short axis methyl substituents by a one atom bridge afforded μ-bridged *syn*-bimanes [7]. These tricyclic heterocycles were generally obtained from the dibromide **17** in reactions with nucleophiles. We repeated Kosower's preparation of μ-(dicarboethoxy)methylene-*syn*-(methylene,methyl)bimane **5** from the dibromide **17** in a reaction with malonic ester [7], and similarly prepared the homologous dimethyl ester **22**. The diester **5** was converted by hydrolysis with decarboxylation to the monocarboxylic acid **23** [7]. Our attempts to convert the acid to its sodium salt were unsuccessful; mild treatment with sodium hydroxide, sodium bicarbonate, sodium alkoxide, or



Compound	*X*	*Cpd*	*X*
5	$C(CO_2C_2H_2)_2$	**50**	S
22	$C(CO_2CH_3)_2$	**51**	SO_2
23	$CHCO_2H$	**52**	$C(CN)_2$
24	NNH_2	**53**	NH
25	$NN{=}C(CH_3)_2$	**54**	$NCOCH_3$
49	NCH_2CH_2OH	**55**	$NCOCF_3$

sodium hydride gave intractable mixtures, in agreement with a known instability of the bimane nucleus toward alkali [6].

By replacing ammonia with hydrazine in Kosower's scheme for converting *syn*-(bromomethyl,methyl)bimane **17** to μ-amino-*syn*-(methylene, methyl)bimane **53** [7] the corresponding N-amino derivative **24** was obtained without competitive formation of the cyclic hydrazine isomer (with an eight-membered ring). The hydrazine **24** was characterized by conversion to its perchlorate salt and to the hydrazone derivative **25** obtained from acetone.

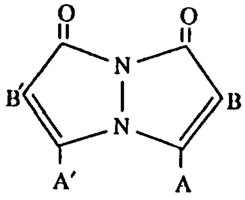
syn-(*Benzo*)- *and* syn-(α-*naphtho*)*bimanes* ***28*** *and* ***36***

Dehydrogenation of the previously reported *syn*-(tetramethylene)bimane (**26**) [6] by treatment with dichlorodicyanobenzoquine (DDQ) afforded both *syn*-(benzo)bimane **28** and the intermediate *syn*-(benzo,tetramethylene)bimane **27**. Attempted dehydrogenation of bimane **26** by treatment with either 1,4-chloranil or palladium (10%) on charcoal was unsuccessful.

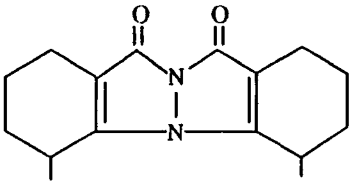
Bromination converted the bimane **26** to a dibromide that was given the tentative assignment of 4,6-dibromo-1,2,3,4,6,7,8,9-octahydro-10*H*,12*H*-indazolo[1,2-*a*]indazol-10,12-dione **29**. Treatment with an excess of DDQ converted the dibromide **29** to *syn*-(benzo)bimane **28**. The formation of a bromo derivative of bimane **28** was not detected.

An alternative approach to the preparation of *syn*-(benzo)bimane **28** that called for dehydration with cyclization of N,N-di-*o*-carboxyphenylhydrazine **32** was abandoned when the corresponding nitrosamine precursor **31** was not obtained by the treatment of di-*o*-carboxyphenylamine **30** [17] with nitrosating agents. A related conversion of N,N'-di-*o*-carboxyphenylhydrazine **33** [(o-$HO_2CC_6H_4NH)_2$] to *anti*-(benzo)bimane **34** was reported in 1916 [18].

syn-(α-Naphtho)bimane **36** was similarly obtained by a dehydrogenation of 5,6,10,-11-tetrahydro-7*H*,9*H*-benz[6,7]indazolo[1,2-*a*]benz[*g*]indazol-7,9-dione **35** by treatment with palladium (10%) on charcoal. The bimane **35** was prepared



Compound	A,B	A',B'
26	$(CH_2)_4$	$(CH_2)_4$
27	$(CH_2)_4$	$(CH)_4$
28	$(CH)_4$	$(CH)_4$
46	$HOCH_2$, CH_3	CH_3, CH_3
47	$CH_3CO_2CH_2$, CH_3	CH_3, CH_3



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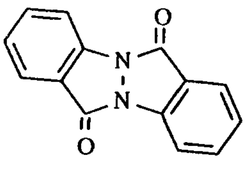
$(o\text{-}HO_2CC_6H_4)_2NX$
30 X = H
31 X = NO
32 X = NH_2



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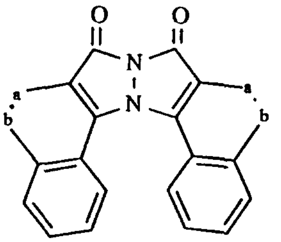
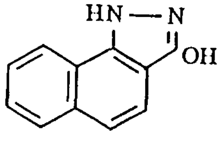


35 a · b = CH_2CH_2
36 a · b = CH=CH



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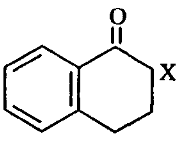
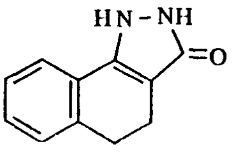


37 X = $CO_2C_2H_5$



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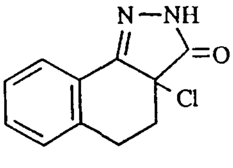

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from ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** [19] by treatment with hydrazine to give 1,2,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **38** followed by chlorination to give 3a-chloro-2,3a,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one **39** and treatment with potassium carbonate. A structure confirmation of the indazolone **38** was provided by its dehydrogenation over palladium to give 1*H*-benz[*g*]-indazol-3-ol **40.** In the absence of an x-ray crystallographic analysis, precluded by inability to obtain a crystalline modification, helicity for bimane **36** was corroborated by an analysis based on molecular modeling. In contrast to the *syn*-(benzo)bimane **28** in which the carbon atoms attached to the axial substitution sites are calculated to lie in the molecular plane, the corresponding carbon atoms in the *syn-(α*-naphtho)bimane **36** are calculated to be displaced by 0.53 Å above and below the mean molecular plane.

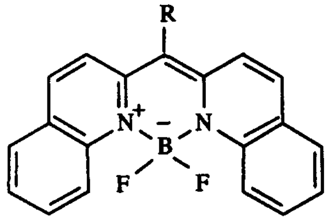
syn-*BIMANE LASER ACTIVITY*

Background Information

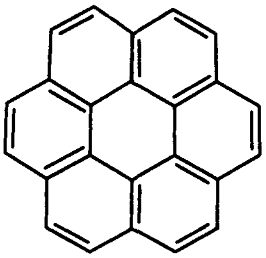
In water *syn*-(methyl,hydrogen)bimane **12** [6] showed fluoroescence λ_{max} 430 nm (Φ = 0.7), T-T absorption λ_{max} 490 nm with a shoulder at λ 420 nm, and no laser activity [20]. For comparison *syn*-(methyl,methyl)bimane **1** in water showed fluorescence λ_{max} 480 nm (Φ = 0.7), the same T-T absorption curve, and broad-band laser activity at λ 504 nm [5a]. It was suggested that a long-axis methyl substituent introduced a red shift solvatochromic effect on the fluorescence of the bimane **1** in water that promoted its laser activity above 500 nm where T-T absorption had steeply declined in intensity [5a]. The lasing efficiency (about 40% as efficient as coumarin 30) [21] was low—presumably a consequence of declining fluorescence intensity in the same spectral region [5a]. An absence of detectable laser activity from the bimane **1** in ethanol or in *p*-dioxane was attributed to solvatochromic shifts in fluorescence λ_{max} to 460 and 420 nm, respectively, where T-T absorption was more intense [5a]. Laser activity for *syn*-(hydrogen, methyl)bimane Type I (A = H, B = CH_3), fluorescence λ_{max} 460 nm (Φ = 0.6) [22], was not investigated; therefore a short-axis methyl substituent effect on laser activity was not directly established.

A study of the polarization of low energy electronic transitions (S-S and T-T) revealed the presence of two differently polarized T-T transitions in the spectral region of fluorescence for *syn*-bimanes. This increased the complexity of both long- and short-axis substituent effects on the T-T absorption and indirectly on the laser activity for *syn*-bimanes [20]. Investigations are planned to unravel these and other polarization effects in bimanes.

Angular *endo*-annelation was found in the laser active "boradiazinium salt" **41** [23] but was not extended to test the possibility of a helical laser dye. That helicity could create an interference with luminescence was shown in an examination of a series of hydrocarbons in which progressive helicity correlated with diminished fluorescent intensity [24]. Presumably laser activity in coronene **42** [25] was enhanced by chromophore planarity. We have herein reported the angular *endo*-annelation of *syn*-bimane into four-ring and six-ring systems.



41 R = 2-isoquinolyl



42

RESULTS AND DISCUSSION

syn-Bimane derivatives offered a promising new source of laser dyes for the spectral region 500–530 nm. An examination of 18 Type I, two Type II, 13 Type III, and four annelated *syn*-bimanes revealed significant laser activity in eight from Types I and II (Table 1) and five from Type III (Table 2). Relative efficiencies, RE (± 10%), in laser power output were determined by comparison with the performance shown by a 7.5 × 10^{-4} M solution in ethanol of coumarin 30 (RE arbitrarily 100). Bimanes **3, 5, 18,** and **22** (Tables 1 and 2) gave RE > 80. Each of these four dyes offered a high quantum fluorescence yield (Φ > 0.7), solvatochromic control of interference from absorption (S-S and T-T), superior photostability, and availability. In addition, dyes **3** and **18** were water soluble.

A replacement of the ester groups in dye **5** (or **22**) with cyano groups offered the strongly fluorescent *μ*-dicyanomethylene-*syn*-(methylene,methyl) bimane **52** (RE 0). A complete inhibition of laser activity in **52** was attributed in part to an electronic interaction between the cyano groups and the nearby chromophore. (In other examples inhibition of luminescence was attributed to a similar interaction between nitro and chromophore

TABLE 1 *syn*-(A,B)Bimanes, Type I and *syn*(A,B)(A′,B′)Bimanes, Type II: Laser Activity in the Region 500–530 nm

Compound[a,b]				*Power Output, P_1 and P_2 (mJ)*			
No.	*A*	*B*	*Solvent*[c]	P_1[d]	*RE*[c] (%)[e]	P_2[f]	*RE* (%)[e]
1	CH_3	CH_3	HFI	2.45	41	5.27	43
2	CH_3	Cl	TFE	1.75	29	5.15	42
3	$CH_3CO_2CH_2$	CH_3	H_2O	4.37	72	10.92	89
4	FCH_2	CH_3	TFE[g,h]	0.31	5	3.0	24
18	$(CH_3O)_2P(O)CH_2$	CH_3	H_2O[i]	4.43	73	10.43	85
20	$HOCH_2$	CH_3	H_2O	3.48	58	8.19	67
No.	*A,B*	*A′B′*					
26	$(CH_2)_4$	$(CH_2)_4$	TFE[j]	0.70	12	2.60	21
46[k]	$HOCH_2$, CH_3	CH_3, CH_3	HFI[m]	0.23	4	2.39	19
47	$CH_3CO_2CH_2$, CH_3	CH_3, CH_3	H_2O[n]	0.7	15	4.98	56

[a] 10^{-3} M.

[b] Fluorescence in the region 435–460 nm with Φ values in the range 0.6–0.9 was reported for compounds *1* [6], *2* [6], *3* [8], *4* [5c], *20* [8], *26* [6], and *46* [7]. See Experimental for compound *18*.

[c] HFI, hexafluoroisopropanol; TFE, trifluoroethanol.

[d] Dye pumped to 5.0 J.

[e] Relative efficiency compared to 100 (arbitrary) for coumarin 30.

[f] Dye pumped to 10.0 J.

[g] Mixed with water (10%).

[h] Laser activity at 435 nm from bimane **4** in dioxane.

[i] Laser activity at 438 nm from bimane **18** in dioxane.

[j] Mixed with water (10%).

[k] Rapid photodecomposition.

[m] Concentration not determined.

[n] 20% HFI.

TABLE 2 *μ*-X-*syn*-(Methylene,methyl)bimanes, Type III: Laser Activity in the Region 500–530 nm

Compound[a,b]			*Power Output, P_1 and P_2 (mJ)*			
No.	*X*	*Solvent*[c]	P_1[d]	RE(%)[e]	P_2[f]	RE(%)[e]
5	$C(CO_2C_2H_5)_2$	HFI	4.76	79	10.00	82
22[h]	$C(CO_2CH_3)_2$	TFE[g]	5.85	97	13.13	107
24	NNH_2	H_2O[i]	2.17	36	6.27	51
50	S	HFI	2.98	49	7.55	61
52	$C(CN)_2$	H_2O[j]	0.17	3	0.4	3
53	NH	H_2O	0	0	1.22	9
55	$NCOCF_3$	TFE[g]	0.33	5	1.6	13

[a] 10^{-3} M.

[b] Fluorescence, λ (Φ): 426 (0.8) for compound **5** and 447 (0.8) for compound **50** were reported [7]. See Experimental for compounds **22**, **24**, and **55**.

[c] HFI, hexafluoroisopropanol; TFE, trifluoroethanol.

[d] Dye pumped to 5.0 J.

[e] Relative efficiency compared to 100 (arbitrary) for coumarin 30.

[f] Dye pumped to 10.0 J.

[g] Mixed with water (10%).

[h] Ref. 7.

[i] Contained perchloric acid. An aqueous solution of the perchlorate salt (Experimental) in water gave no laser activity when pumped to 5.0 J and 0.43 mJ (RE 3.5%) when pumped to 10.0 J.

[j] Mixed with 20% HFI.

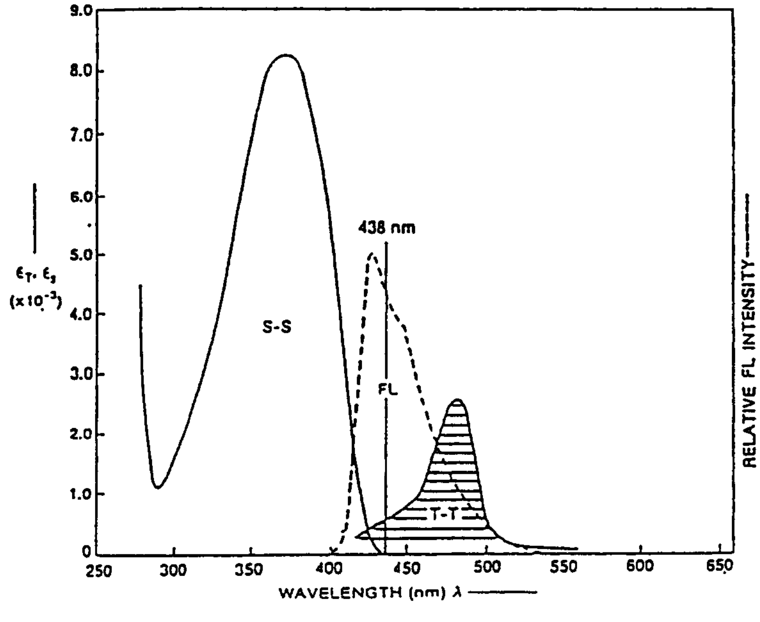


FIGURE 1 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 438 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18** in *p*-dioxane. The T-T absorption spectrum was recorded at 77°K, employing a 2 × 10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1 × 10^{-3} molar) spectra were recorded with *p*-dioxane as solvent.

groups. [3].) The conspicuous absence of a cyano derivative in current lists of dyes [2–4] was taken an an indication that the cyano group within the dye molecule generally quenched laser activity.

The diphosphonate **18** was noted for a solvatochromic effect that shifted its fluorescence maximum from 425 nm in dioxane to 460 nm in water without shifting T-T absorption at about 480 nm to afford laser activity at 438 nm in one and at 514 nm in the other solvent (Figures 1 and 2). In water the solubility of the diphosphonate **18** (0.2 M) surpassed coumarin 30 (less than 10^{-4} M) but was 20% less power efficient (Figure 3) when each was pumped to 4.5 J. The diphosphonate **18** showed good photostability; however, after exposure in methanol to irradiation at 250 nm for 1 week it was completely converted to unidentified material. Under similar prolonged irradiation *syn*-(methyl, methyl)bimane **1**, a yellow solid, was converted to an unknown colorless powder.

Dyes that showed RE 20-80 included the bimanes **1** [5a], **2** [5b], **4** [5b], **20**, and **26** (Table 1); and bimanes **24** and **50** (Table 2). A long-axis alkyl substituent effect that was discovered for the methyl group in bimane **1** [5a] was greatly diminished in *syn*-(tetramethylene)bimane **26** and was ineffective in bimanes **6–9** that were laser inactive. The performance (RE 42) that was characteristic of *syn*-(methyl,chloro)bimane **2**, Φ 0.8 (Table 1) was not shared with *syn*-(carboethyoxy,chloro)bimane **45**, Φ 0.1, (inactive) and *syn*-(phenyl,chloro)bimane **44**, Φ 0.6, (inactive). Although these results are in line with the general requirement for the presence of strong fluorescence, the laser inactivity in the latter example was attributed in part to interference from an assumed T-T absorption (phenyl group).

The results obtained from *syn*-(hydroxymethyl,methyl)bimane **20**, Φ 0.60, (RE 67) and *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane **46**, Φ

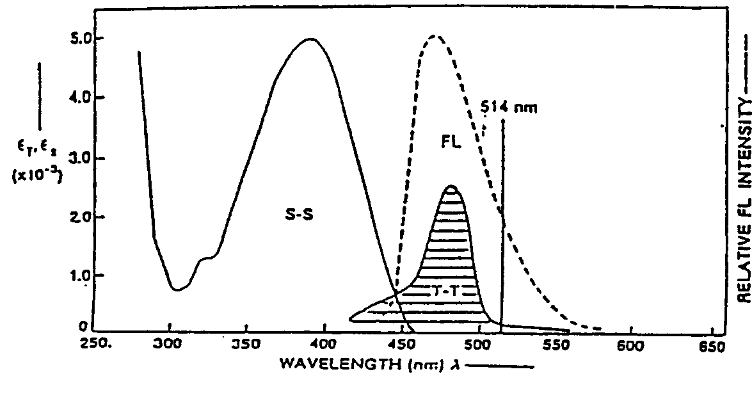


FIGURE 2 Absorption (S-S and T-T), fluorescence (FL), and the center of broad-band laser activity at 514 nm for *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18**. The T-T absorption spectrum was recorded at 77°K, employing a 2 × 10^{-4} molar solution of 2-methyltetrahydrofuran. The S-S and Fl (1 × 10^{-3}) spectra were recorded with water as a solvent.

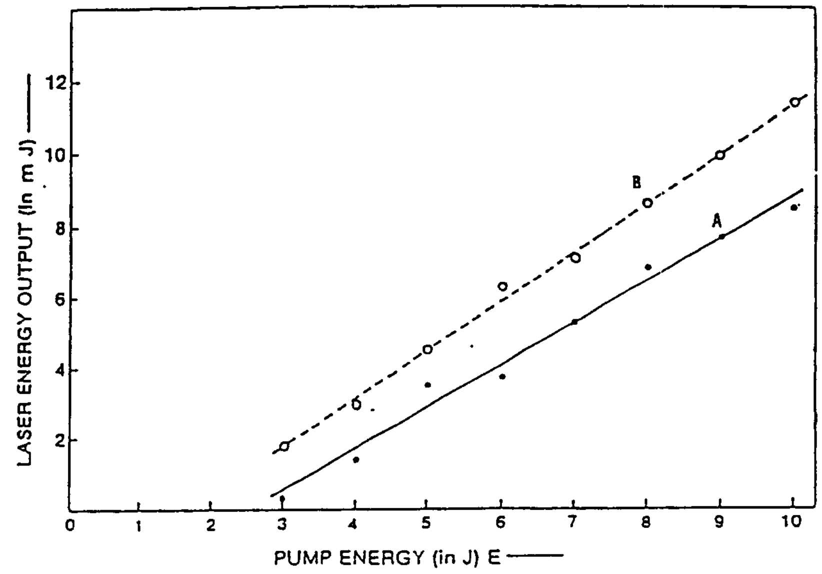


FIGURE 3 Laser energy output (mJ) as a function of flashlamp pump energy (J) of (A) *syn*-(dimethoxyphosphinylmethyl,methyl)bimane **18**, 1 × 10^{-3} M in water and (B) coumarin 30, 7.5 × 10^{-4} M ethanol.

0.80, (RE 19) (Table 1) appeared to be in conflict; however, a decrease in the laser activity of the alcohol **46** was attributed to its rapid photodecomposition, a property not shared with the other bimanes in this report. Although a lower performance rating for the glycol **20** (RE 67), relative to its diacetate ester **3** (RE 89), could be attributed to self-quenching brought about by dye aggregation as a result of hydrogen bonding, a parallel improvement in the performance of the alcohol **46** (RE 19) on conversion to its acetate ester **47** (RE < 19) was not observed.

Our results indicated that bimane laser dyes with μ-heteroatom bridges did not afford superior performances. No laser activity was detected from μ-amino-*syn*-(methylene,methyl)bimane **53**, its N-β-hydroxyethyl derivative **49**, and its N-acetyl derivative **54.** The N-trifluoroacetyl derivative **55** (RE 13) and the N-amino derivative **24** (RE 51) (Table 2) showed weak laser activity. There was some improvement shown by μ-thia-*syn*-(methylene,methyl)bimane **50** (RE 61); however, μ-sulfono-*syn*-(methylene,methyl)bimane **51** was laser inactive. Laser inhibition as a result of an electronic interaction between amino, thia, or sulfono bridges and the nearby chromophore was assumed.

Strong T-T absorption for *syn*-(benzo)bimane **28** was shown to interfere throughout the fluorescence spectral region [20] and presumably quenched laser activity. A similar quenching effect was assumed for the related bimanes **27** and **35.** The absence of laser activity in bimanes **17, 29, 44,** and **45** was partially attributed to the heavy atom effect. A low fluorescence quantum yield, Φ 0.1, for laser inactive *syn*-(α-naphtho)bimane **36** (compare Φ 0.9 for *syn*-(benzo)bimane **28**) was attributed to further disruption in the planarity of the bimane chromophore that was presumably brought about by helicity.

EXPERIMENTAL

Spectral data were obtained from the following instruments: Pye–Unicam SP 200 IR, Varian A-60 and JEOL FX Q NMR, Hewlett-Packard 5985 (70 eV) (GC-MS), Beckman DU (UV), and a Perkin-Elmer LS-5B Luminescence Spectrometer. A dye laser was constructed at the Naval Ocean Systems Center [26]. It operated in the nonflowing (static) mode and had no tuning capability. The dye cell (2.5 mm diam., 50 mm long) had an elliptical cavity configuration of small eccentricity. The flashlamp pulser, EG & G model FX 139C-2, had a rise time of 200 ns, half-width length of 600 ns, and input energy of 2 J at 6.32 kV, 5 J at 10.00 kV, 7.2 J at 12.00 kV, and 10 J at 14.14 kV [5a]. Laser energy outputs were measured with an accuracy of ±5% by a Scientech 365 power and energy meter [5c]. Laser activities are described in Tables 1 and 2.

For each product the IR spectrum agreed with the literature data and/or supported the assigned structure. Each recorded UV absorption was restricted to the highest wavelength. H NMR (60 MHz) spectra were run in $CDCl_3$ with tetramethylsilane as an internal standard. ^{13}C NMR were recorded at 22.5 MHz with the deuterated solvent as an internal reference. The central peak of the solvent multiplet signal was assigned: δ 77.00 ($CDCl_3$), 39.50 ($(CD_3)_2(SO)$). Fluorescence quantum yields were determined by reference to *syn*-(methyl, methyl)bimane **1**, Φ 0.72 [6], *syn*-(benzo)bimane **28**, Φ 0.9 [27], and/or quinine sulfate, Φ 0.55. The latter reference was abandoned for several determinations when it led to erratic results. The mass spectra were electron impact (70 eV). Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analyses were obtained from Midwest Micro Lab, Indianapolis, IN, and Galbraith Laboratories, Knoxville, TN. Solvents were removed by rotary evaporation under reduced pressure unless indicated otherwise. Column chromatography was performed on silica gel (various grades). Triplet extinction coefficients over the laser action spectral region of the dye were measured at the temperature of liquid nitrogen by equipment previously described [28] using McClure's method [29]. Molecular mechanics calculations were performed on a MicroVAX 2000 computer with Evans and Sutherland PS390 graphics display using the BIOGRAF [30] software package. The force field parameters were taken from the MM2 set [31].

Solvents, reagents, and starting materials that were obtained from the Aldrich Chemical Company, Milwaukee, WI included acetic anhydride, acetone, acetonitrile, acryloyl chloride, alumina, ammonium chloride, benzaldehyde, benzene, bromine, β-bromoethyl acetate, carbon tetrachloride, celite, cetyltrimethylammonium Bromide *m*-chloroperbenzoic acid, chloroform-d, dichlorodicyanobenzoquinone (DDQ), dichloromethane, diethyl acetylsuccinate, diethyl carbonate, diethyl ethoxymethylenemalonate, N,N-disopropylethylamine, N,N-dimethylformamide (DMF), dimethyl sulfoxide-d_6 (DMSO-d_6), *p*-dioxane, 18-crown-6-ether, ethanol, ethyl acetate, ethyl benzylacetoacetate, hexane, hexafluoroisopropanol, hydrazine hydrate, iodobenzene diacetate, isopropanol, methanol, α-methyltetrahydrofuran, nitric acid, palladium (10% on charcoal), perchloric acid, peroxytrifluoroacetic acid, petroleum ether, potassium bromide, potassium *tert*-butoxide, potassium carbonate, potassium fluoride, potassium superoxide, silica gel (230–400 mesh, 60 Å), sodium bicarbonate, sodium hydride, sodium hydroxide, sodium sulfate, tetrahydrofuran (THF), α-tetralone, *p*-toluenesulfonic acid, triethylamine, trifluoroacetic anhydride, trifluoroethanol, and trimethyl phosphite. Coumarins 6, 30, 120, and 314, rhodamine 6G, sulforhodamine B and thin layer chromatography sheets were obtained from Eastman Kodak Co., Rochester, NY. Chlorine was obtained from Matheson Gas Products, Secaucus, NJ. Nitrogen was obtained from Air Products and Chemicals, Allentown, PA. Hydrogen peroxide (90%) was obtained from Shell Chemical Company, Houston, TX.

The following compounds were prepared according to the directions cited: bimanes type I: *syn*-(A,B)bimanes where (A,B) was (methyl,hydrogen) in **12** [6], (methyl,methyl) in **1** [6], (bromomethyl,methyl) in **17** [6, 8], (hydroxymethyl,methyl) in **20** [8], (tetramethylene) in **26** [6], (methyl,phenyl) in **43** [6], (phenyl,chloro) in **44** [6], and (carboethoxy,chloro) in **45** [22]; bimanes type II: *syn*-(hydroxymethyl,methyl)(methyl,methyl)bimane **46** [6]; bimanes type III: μ-X-*syn*-(methylene, methyl)bimanes where X was dicarboethoxymethylene in **5** [7], dicarbomethoxymethylene in **22** [7], carboxymethylene in **23** [7], thia in **50** [7], sulfono in **51** [7], dicyanomethylene in **52** [7], amino in **53** [7], and acetylamino in **54** [7]; bimanes type IV: *anti*-(methyl,hydrogen)bimane **13** [6] and *anti*-(amino,hydrogen)bimane **11** [13]; miscellaneous: 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one **10c** [32], 4-β-acetoxyethylethyl-3-methyl-2-pyrazolin-5-one [33], and ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** [19].

4-Benzyl-4-chloro-3-methyl-2-pyrazolin-5-one ***10b***

Hydrazine hydrate (10.5 g, 0.21 mol) in methanol (20 mL) was added slowly with stirring to ethyl benzylacetoacetate (44.0 g, 0.2 mol) in methanol (200 mL). The mixture was heated at 65°C for 1 h and cooled to bring about the precipitation of 3-methyl-4-benzyl-2-pyrazolin-5-one that recrystallized from ethanol as a colorless solid, 32.0 g (85%), mp 230–231°C (lit. [34] 232°C); H NMR ($CDCl_3$): δ 2.0 (s, 3 H, CH_3), 3.6 (s, 2 H, CH_2), and 7.2 (s, 5 H, C_6H_5). A solution of the pyrazolinone (32.0 g, 0.17 mol) in dichloromethane (300 mL) was treated with a stream of chlorine gas until the solid phase disappeared and the solution became yellow. Traces of chlorine were removed by purging with a stream of nitrogen. The solvent was removed to leave a yellow oil that recrystallized from benzene to give the chloropyrazolinone **10b** as a yellow solid, 32.5 g (86%); mp 75–76°C; H NMR ($CDCl_3$): δ 2.1 (s, 3 H, CH_3), 3.3 (d, 2 H, CH_2), 7.2 (s, 5 H, C_6H_5), 8.9 (broad, 1 H, NH). Anal. calcd for $C_9H_{11}N_2OCl$: C, 59.32; H, 4.94; N, 12.58;. Cl, 15.95. Found: C, 59.26; H, 5.08;. N, 12.79; Cl, 15.90.

syn-*(Methyl,benzyl)bimane* ***6***

The prepared mixture (10 g) of potassium fluoride and neutral alumina (2 : 3 by wt) was added to the chloropyrazolinone **10b** (1.0 g, 5 mmol) in dichloromethane (100 mL) at 10°C and the mixture was stirred for 1 h. Filtration and concentration of the mother liquor left a residue that recrystallized from carbon tetrachloride to give the bimane **6** as a yellow crystalline solid, 0.5 g (62%); mp 124–125°C; H NMR ($CDCl_3$): δ 2.25 (s, 6 H, CH_3), 3.6 (s, 4 H, CH_2), 7.25 (s, 10 H, C_6H_5); ^{13}C NMR ($CDCl_3$): δ 159.78 (CO); 145.99 ($O{=}C{-}C{=}\mathbf{C}$); 138.58, 128.43, 128.04, and 126.22 (C_6H_5); 115.56 ($O{=}C{-}\mathbf{C}{=}C$); 27.51 (CH_2); 11.71 (CH_3). UV (CH_3CN): λ (ε) 375 (7916); fluorescence (dioxane): λ (Φ) 417 (0.8); EI-MS: 344 (M^+). Anal. calcd for $C_{22}H_{20}N_2O_2$: C, 76.74; H, 5.81; N, 8.13. Found: C, 76.52; H, 5.80; N, 8.25.

When the reaction was catalyzed by potassium carbonate a mixture (1 : 1) (87%) of the bimane **6** and its *anti* isomer **A6** was obtained.

syn-(*Methyl,carboethoxymethyl*)*bimane* **7**

To 3-methyl-4-carboethoxymethyl-4-chloro-2-pyrazolin-5-one (4.4 g, 20 mmol) in dichloromethane (200 mL) a prepared mixture (44 g) of potassium fluoride and neutral alumina (2 : 3 by wt) was added at 25°C with stirring that was continued for 1 h. After filtration the mother liquor was concentrated to leave a brown solid that was purified by flash chromatography from a column of silica gel (dichloromethane) to give *anti*-(methyl,carboethoxymethyl)bimane **A7** as a colorless solid, 1.2 g (36%), mp 183–184°C (lit. [32] mp 180°C), followed by the *syn* isomer **7** as a pale-yellow solid, 0.5 g (15%); mp 146–147°C; H NMR ($CDCl_3$): δ 1.27 (t, 6 H, CH_3), 2.4 (s, 6 H, CH_3), 3.3 (s, 4 H, CH_2), 4.13 (q, 4 H, CH_2); UV (CH_3CN): λ (ε) 370 (7303); fluorescence (ethanol): λ (Φ) 420 (0.8); EI-MS: 336 (M^+). Anal. calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.92; N, 8.33. Found: C, 56.91; H, 5.71; N, 8.58. When an attempt to repeat the preparation with potassium carbonate as the catalyst was made the starting material was partially converted to a mixture of bimanes **3** and **A3** after 20 h at 25°C.

4-β-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d**

Chlorine gas was bubbled into a suspension of 4-β-acetoxyethyl-3-methyl-2-pyrazolin-5-one (15.0 g, 80 mmol) in dichloromethane (500 mL) until the suspension dissolved to give a yellow solution. The solution was stirred for an additional 30 minutes. Excess chlorine and the solvent were removed under reduced pressure to give a yellow residue, which was recrystallized from a mixture of hexane and carbon tetrachloride to give 4-β-acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d** as a colorless crystalline solid, 13.5 g (76%); mp 94–95°C; H NMR ($CDCl_3$): δ 2.00 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.47 (t, 2 H, CH_2), 4.05 (t, 2 H, CH_2), 9.35 (br, 1 H, NH). Anal. calcd for $C_8H_{11}N_2O_3Cl$: C, 43.95; H, 5.07; N, 12.81; Cl, 16.22. Found: C, 43.83; H, 5.04; N, 12.89; Cl, 16.66.

syn-(*Methyl, β-acetoxyethyl*)*bimane* **8**

4-β-Acetoxyethyl-4-chloro-3-methyl-2-pyrazolin-5-one **10d** (5.0 g, 23 mmol), potassium carbonate (10.0 g, 72 mmol), and water (2 mL) were added to dichloromethane (300 mL). The resulting suspension was stirred vigorously for 4 h. The reaction was monitored with thin-layer chromatography (ethyl acetate). Celite 545 (10 g) was then added, and the resulting mixture was passed through a short silica gel column (dichloromethane, 100 mL). The solvent was removed to give a yellow residue which was recrystallized from ethyl acetate to give 2.7 g (70%) of the bimane **8**, mp 134–135°C; H NMR ($CDCl_3$): δ 2.03 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.62 (t, 2 H, CH_2), 4.15 (t, 2 H, CH_2); UV (H_2O): λ (ε) 384 (6048); fluorescence (dioxane): λ (Φ) 457 (0.8). Anal. calcd for $C_{16}H_{20}N_2O_6$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

syn-(*Methyl,2-hydroxyethyl*)*bimane* **9**

syn-(Methyl,acetoxyethyl)bimane **8** (1.0 g, 3 mmol) and toluenesulfonic acid (20 mg) was dissolved in methanol (50 mL). The solution was heated at 60°C for 2 days, and the reaction was monitored with thin-layer chromatography (ethyl acetate). The solvent was removed to give a yellow residue which recrystallized in acetonitrile and dimethylformamide to give 0.30 g (40%) of the bimane **9** mp 186.5–188°C; H NMR ($CDCl_3$-DMSO-d_6): δ 2.33 (t, 2 H, CH_2) 2.39 (s, 3 H, CH_3), 3.39 (t, 2 H, CH_2), 3.77 (br, 1 H, OH); UV (H_2O): λ (ε) 317 (23,048); fluorescence (dioxane): λ (Φ) 464 (0.5). Anal. calcd for $C_{12}H_{16}N_2O_4$: C, 57.13; H, 6.39; N, 11.10. Found: C, 57.08; H, 6.57; N, 10.99.

Ethyl 4-chloro-5-oxo-2-pyrazoline-4-carboxylate **10e**

Hydrazine hydrate (5.5 g, 0.1 mol) in ethanol (20 mL) was added with stirring to a solution of diethyl ethoxymethylenemalonate (21.6 g, 0.1 mol) in ethanol (200 mL). The mixture was heated at 80°C for 18 h and cooled. Ethyl 2-pyrazolin-5-one-4-carboxylate precipitated and recrystallized from ethanol as a colorless crystalline solid, 7.5 g (48%); mp 177–178°C (dec); H NMR (DMSO- d_6): δ 1.2 (t, 3 H, CH_3), 4.2 (q, 2 H, CH_2), 7.9 (s, 1 H, CH); EI-MS: 156 (M^+). Anal. calcd for $C_6H_8N_2O_3$: C, 46.15; H, 5.12; N. 17.94. Found: C, 46.25; H, 5.13; N, 17.93. The pyrazolinone (5.0 g, 32 mmol) in dichloromethane (200 mL) was treated with a stream of chlorine gas at 25°C until the solid phase disappeared and the solution became yellow. Excess chlorine was purged with a stream of nitrogen. Removal of the solvent left the chloropyrazolinone **10e** or an isomer that recrystallized from benzene as a yellow solid, 5.5 g (90%); mp 103–105°C; H NMR ($CDCl_3$): δ 1.3 (t, 3 H, CH_3), 4.4 (q, 2 H, CH_2), 7.4 (s, 1 H, CH), and 9.6 (broad, 1 H, CH). Anal. calcd for $C_6H_7N_2O_3Cl$: C, 37.79; H, 3.79; N, 14.69; Cl, 18.68. Found: C, 37.87; H, 3.57; N, 14.63; Cl, 18.72. Attempts to convert the product **10e** (or isomer) under the catalysis of either potassium carbonate, or N,N-diisopropylethylamine, or potassium fluoride on alumina, or sodium hydride in tetrahydrofuran to *syn*-(hydrogen,carboethoxy)bimane were unsuccessful.

anti-(*Methyl,nitro*)(*methyl,hydrogen*)*bimane* ***16***

After a mixture of nitric acid (90%, 0.20 mL) and acetic anhydride (0.75 mL) was stirred at 0°C for 15 m, *anti*-(methyl,hydrogen)bimane **13** (0.16 g, 1.0 mmol) was added slowly. The mixture was stirred at 0°C for 30 m and poured onto crushed ice to precipitate the nitrobimane **16** as an orange solid, 0.12 g (57%), mp 196°C (dec) (acetone). H NMR ($CDCl_3$): δ 2.6 (s, 3 H, CH_3), 3.0 (s, 3 H, CH_3), and 5.5 (s, 1 H, CH); EI-MS: 209 (M^+). Anal. calcd for $C_8H_7N_3O_4$: C, 45.94; H, 3.37; N, 20.09. Found: C, 45.62; H, 3.19; N, 19.59.

Attempts to extend the nitration reaction to *syn*-(methyl,hydrogen)bimane **12** gave intractable mixtures. A trace amount of solid was thought to be a *syn*-isomer of bimane **16** since the mass spectrometric analysis showed EI-MS 209 (M^+).

anti-(*Amino,nitro*)*bimane* ***15***

Following the above procedure *anti*-(amino,hydrogen)bimane **11** (0.4 g, 2.4 mmol) in a mixture of nitric acid (90%, 0.7 mL) and acetic anhydride (2.0 mL) at 0°C with stirring for 30 min gave the dinitrobimane **15** as a red orange solid, 0.56 g (91%), mp 318°C (dec) (acetone). ^{13}C NMR (DMSO-d_6): δ 107.8, 151.3, and 153.7; EI-MS 256 (M^+). Anal. calcd for $C_6H_4N_6O_6$: C, 28.13; H, 1.56; N, 32.81. Found: C, 28.07; H, 1.57;. N, 32.07.

Oxidation of Aminobimanes

The diaminobimane **11** in a mixture of trifluoroacetic anhydride and hydrogen peroxide (90%) was converted to an intractable yellow gum. The diaminodinitrobimane **15** was unaffected by *m*-chloroperbenzoic acid, or peroxytrifluoroacetic acid, or iodobenzene diacetate.

A slurry of the diaminodinitrobimane **15** (0.8 g, 3.1 mmol), 18-crown-6 ether (0.15 g), and potassium superoxide (1.0 gm 14.1 mmol) in benzene was stirred for 17 h at 25°C under nitrogen. Addition of water gave a clear yellow aqueous layer that was acidified (dilute hydrochloric acid) to precipitate a trace amount of solid, mp > 300°C, that was discarded. Addition of ethanol to the filtrate caused the precipitation of a potassium salt as a colorless solid, 0.15 g (13%), mp 150°C (dec) (aqueous ethanol). Anal. calcd for $C_6N_4O_8K_2 \cdot 1.5\ H_2O$: C, 19.94; H, 0.83; N, 15.51. Found: C, 19.82; H, 0.71; N, 15.96.

syn-(*Dimethoxyphosphinylmethyl,methyl*) *bimane* ***18***

A mixture of *syn*-(bromomethyl,methyl)bimane **17** (7.0 g, 0.2 mmol) and trimethyl phosphite (10 mL) was heated at 115°C for 30 m as it became homogeneous and solidified. After trituration with hexane (50 mL) the mixture was taken up in ethyl acetate. The bimane **18** separated as a yellow crystalline solid, 6.3 g (78%); mp 224–225°C; H NMR ($CDCl_3$): δ 1.87 (d, 6 H, J = 4 Hz, CH_3), 3.72 (d, 4 H, J = 22 Hz, CH_2), 3.75 (d, 12 H, J = 10 Hz, OCH_3); ^{13}C NMR ($CDCl_3$): δ 159.52 (CO), 140.40 and 139.95 (O=C—C=**C**), 114.91 and 114.58 (O=C—**C**), 53.52 and 53.19 (PO-CH_3), 26.34 and 20.09 (CH_2), and 6.83 (CH_3); UV (CH_3CN): λ (ε) 380 (6984); fluorescence (dioxane): λ (Φ) 417 (0.7); EI-MS: 408 (M^+). Anal. calcd for $C_{14}H_{22}N_2O_8P_2$: C, 41.17; H, 5.39; N, 6.86; P, 15.19. Found: C, 40.95; H, 5.35; N, 6.80; P, 15.41.

syn-(*Styryl,methyl*)*bimane* ***19***

A mixture of the diphosphonate **18** (1.0 g, 2.5 mmol), potassium carbonate (1.4 g, 10 mmol), benzaldehyde (0.5 g, 5 mmol), and water (2 mL) was heated at 100°C for 4 h, cooled, combined with dichloromethane (200 mL), and washed with water (2 × 50 mL). The organic layer was dried (sodium sulfate) and concentrated to leave a brown solid that recrystallized from methanol to give the bimane **19** as a yellow crystalline solid, 0.3 g (29%); mp 214–215°C; H NMR (DMSO-d_6): δ 2.1 (s, 6 H, CH_3), 7.3–7.8 (m, 14 H, C_6H_5CH=CH); ^{13}C NMR (DMSO-d_6): δ 161.36 (CO); 149.92 (O=C—C=**C**); 140.68 (C_6H_5**C**=C), 114.67 and 112.50 (C_6H_5C=**C**—C=**C**—C=O); 135.09, 129.68, 128.72, and 127.42 (C_6H_5); 8.02 (CH_3); UV (CH_3CN): λ (ε) 400 (2530); fluorescence (dioxane): λ (Φ) 428 (0.2); EI-MS: 368 (M^+). Anal. calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.01; H, 5.52; N, 7.53.

To a slurry of potassium t-butoxide (0.8 g, 7.8 mmol) in N,N-dimethylformamide (DMF) (100 mL) the diphosphonate **18** (1.0 g, 2.5 mmol) in DMF (25 mL) was added with stirring under nitrogen at 25°C over a period of 2 h, heated at 70°C for 3 h, cooled, and treated with saturated aqueous ammonium chloride (10 mL). DMF was removed by distillation. The residue was treated with dichloromethane (200 mL), washed with water (2 × 50 mL), dried (sodium sulfate), and concentrated to give a brown solid that afforded the bimane **19** as a yellow crystalline solid, 0.22 g (25%), mp 214–215°C, after purification from methanol.

syn-(*Acryloxymethylene,methyl*)*bimane* ***21***

Triethylamine (3.6 g, 36 mmol) and acryloyl chloride (3.4 g, 36 mmol) were added separately to *syn*-(hydroxymethyl,methyl)bimane **20** (2.0 g, 9 mmol) in DMF (50 mL) with stirring at 25°C over a period of 48 h. The mixture was combined with water (200 mL), extracted with chloroform (3 × 100 mL), washed with aqueous sodium bicarbonate (5%) (30 mL), dried (sodium sulfate), and concentrated to leave a dark brown solid. Purification by flash chromatographic separation from a column of silica gel (80 g, chloroform) gave the bimane **21** as a yellow solid, 0.65 g (22%); mp 121–122°C; H NMR ($CDCl_3$): δ 1.9 (s, 6 H, CH_3), 5.2 (s, 4 H, OCH_2), and 5.8–6.6 (m, 6 H, $CH_2{=}CH$); UV (CH_3CN): λ (ε) 385 (7552); fluorescence (dioxane): λ (Φ) 432 (0.6); EI-MS: 332 (M^+). Anal. calcd for $C_{16}H_{16}N_2O_6$: C, 57.83; H, 4.81; N, 8.43. Found: C, 57.38; H, 4.79; N, 8.07.

syn-*(Acetoxymethyl,methyl)(methyl,methyl) bimane* ***47***

Bromine (1.25 g, 7.8 mmol) in dichloromethane (25 mL) was added dropwise to *syn*-(methyl,methyl)bimane (1.5 g, 7.8 mmol) in dichloromethane (50 mL) at 25°C over a period of 1 h. The solution was stirred for 30 min, and the solvent was removed to leave a red residue that was dissolved in dichloromethane (40 mL). The solution was mixed with aqueous potassium acetate (2 M, 30 mL) that contained cetyltrimethylammonium bromide (300 mg) and stirred for 18 h in the dark. The organic layer was separated, washed with water, and dried (anhydrous sodium sulfate). The solvent was then removed, and the yellow residue gave 0.78 g (40%) of *syn*-(acetoxymethyl,methyl)(methyl,methyl)bimane as a yellow crystalline solid: mp 185–186.5°C (ethyl acetate); H NMR ($CDCl_3$) δ 1.82 (s, 3 H, CH_3), 1.94 (s, 3 H, CH_3), 2.14 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 5.04 (s, 2 H, CH_2); UV (dioxane): λ (ε) 373 (6836). Anal. calcd for $C_{12}H_{14}N_2O_4$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.31; H, 5.63; N, 11.38.

*μ-Aminoimino-*syn*(methylene,methyl)bimane* ***24***

Hydrazine hydrate (0.5 g, 10 mmol) in acetonitrile (10 mL) was added to a solution of *syn*-(bromomethyl,methyl)bimane **17** (0.7 g, 2 mmol) in acetonitrile (25 mL) with stirring at 25°C. The reaction mixture contained a colorless precipitate after 10 m that was collected by filtration after the mixture was diluted with water. The precipitate was triturated with acetonitrile and dried and recrystallized from DMF to give the hydrazine **24** as a yellow solid, 0.3 g (68%); mp 220–221°C (dec); H NMR (trifluoroacetic acid): δ 1.8 (s, 6 H, CH_3), 4.5 (s, 4 H, CH_2); ^{13}C NMR (trifluoroacetic acid): δ 165.70 (CO), 148.50 (O=CC=**C**), 116.6 (0=C—**C**=C), 48.3 (CH_2), 5.4 (CH_3); UV (CH_3CN): λ (ε) 335 (5700); fluorescence(dioxane): λ (Φ): 419 (0.1); EI-MS: 220 (M^+). Anal. calcd for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.45, N, 25.45. Found: C, 54.33; H, 5.48; N, 25.33. The monoperchlorate derivative was prepared in ethanol as a yellow solid, 85%, mp 182–183°C (dec); H NMR (D_2O): δ 1.8 (s, 6 H, CH_3), 4.03 (s, 4 H, CH_2); UV (H_2O): λ (ε) 339 (4611); fluorescence (water): λ (Φ) 460 (0.1); EI-MS: 220 (M^+-$HClO_4$). Anal. calcd for $C_{10}H_{13}N_4O_6Cl \cdot 1.5\ H_2O$: C, 34.53; H, 3.74; N, 16.14; Cl, 10.21. Found: C, 34.59; H, 4.28; N, 16.28; Cl, 10.41.

The hydrazine **24** combined with acetone to give the hydrazone **25** (85%); mp 182–183°C; H NMR ($CDCl_3$): δ 1.8 (s, 6 H, CH_3), 2.0 [d, 6 H, $C(CH_3)_2$], 3.8 (s, 4 H, CH_2); UV (CH_3CN): λ (ε) 339 (6932); fluorescence (dioxane): λ (Φ): 420 (0.15); EI-MS: 260 (M^+). Anal. calcd for $C_{13}H_{16}N_4O_2$: C, 60.00; H, 6.15; N, 21.53. Found: C, 59.85; H, 6.09; N, 21.46.

*N-Trifluoroacetyl μ-amino-*syn*-(methylene,methyl)bimane* ***55***

A suspension of μ-amino-*syn*-(methylene,methyl) bimane **53** (0.50 g, 2.4 mmol) in trifluoroacetic anhydride (7 mL) was stirred at 25°C for 2 h as a pale yellow precipitate appeared. The solvent was removed and the yellow residue recrystallized from a mixture of ethyl acetate and acetonitrile (1 : 1, 10 mL) to give the amide **55** as a colorless crystalline solid (0.30 g, 42%): mp 173–174°C; H NMR ($CDCl_3$) δ 1.86 (s, 3 H, CH_3), 4.78 (s, 2 H, CH_2); UV (CH_3CN): 331 nm (ε 6309); fluorescence (dioxane): λ (Φ) 418 (0.8); EI-MS: 301 (M^+). Anal. calcd for $C_{12}H_{10}N_3O_3F_3$: C, 47.85; H, 3.35; N, 13.95; F, 18.92. Found: C, 47.74; H, 3.34; N, 13.89; F, 18.73.

syn-*Benzobimane* ***28***

A solution of *syn*-(tetramethylene)bimane **26** (1.2 g, 5.0 mmol) in dioxane (50 mL) was treated with DDQ (2.3 g, 10.0 mmol). The solution was heated at 100°C for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane). After cooling a yellow precipitate was removed by filtration and the solvent was concentrated to give a dark brown residue which was redissolved in a minimal amount of dichloromethane and purified by chromatography (silica gel column, dichloromethane). The first fraction contained *syn*-(benzo) bimane **28** as a yellow solid (0.25 g, 29%), mp 308–310°C; H NMR ($CDCl_3$): δ 7.3–8.0 (m); UV (CH_3CN): λ (ε) 420 (6910); fluorescence (50% aqueous ethanol): λ (Φ) 428 (0.9) (reference quinine sulfate Φ 0.55) [27]; EI-MS: 236 (M^+). Anal. calcd for $C_{14}H_8N_2O_2$: C, 71.18; H, 3.41; N, 11.86. Found: C, 71.11; H, 3.41; N, 11.79. The following fraction contained *syn*-(benzo)(tetramethylene)bimane **27** (0.51 g, 58%) as a yellow solid, mp 226–227°C; H NMR ($CDCl_3$): δ 1.88 (m, 4 H), 2.32 (m, 2 H), 2.80 (m, 2 H), 7.10–7.90 (m, 4 H); UV (CH_3CN): λ (ε) 390 (8400); fluorescence (dioxane): λ (Φ) 435 (0.4); EI-MS: 240 (M^+). Anal. calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.87; H, 4.92; N, 11.56. *syn*-(Tetramethylene)bimane **26** (0.30 g) was recovered in the final fraction. When five equivalents of DDQ were employed all of the starting material was converted: *syn*-(benzo)bimane **28** (0.85 g, 72%) was obtained and only a trace amount of *syn*-(benzo) (tetramethylene)bimane **27** was detected by thin-layer chromatography.

*4,6-Dibromo-1,2,3,4,6,7,8,9-octahydro-10*H*, 12*H*-indazolo[1,2-*a*]indazol-10,12-dione* **29**

A solution of bromine (1.6 g, 10.0 mmol) in dichloromethane (20 mL) was added dropwise in the dark to a solution of *syn*-(tetramethylene)bimane **26** (1.2 g, 5.0 mmol) in dichloromethane (30 mL). The reaction mixture was stirred for 15 h as a deep-red solution gradually changed to orange. The solution was washed (aqueous sodium bicarbonate), dried (magnesium sulfate), concentrated, and the residue recrystallized from acetonitrile to give the dibromoindazoloindazoldione **29** as a yellow crystalline solid, 1.85 g (92%); mp 142–143°C; H NMR ($CDCl_3$): δ 1.85–2.67 (m, 12 H), 5.57 (m, 2 H); EI-MS: 402 (M^+). Anal. calcd for $C_{14}H_{14}N_2O_2Br_2$: C, 41.82; H, 3.51; N, 6.97; Br, 39.74. Found: C, 41.57; H, 3.43, N, 6.87; Br, 39.66.

DDQ (1.1 g, 5.0 mmol) and the indazoloindazoldione **29** (0.4 g, 1.0 mmol) were dissolved in dioxane (50 mL). The solution was heated at reflux for 24 h as the reaction was monitored with thin-layer chromatography (dichloromethane) until the starting material **29** was consumed. *syn*-(Benzo)bimane **28**, the major product, was detected by thin layer chromatography.

*1,2,4,5-Tetrahydro-3*H*-benz[*g*]indazol-3-one* **38**

Hydrazine monohydrate (10.0 g, 0.2 mol) was added dropwise to a solution of ethyl 1,2,3,4-tetrahydro-1-oxo-2-naphthoate **37** (43.6 g, 0.2 mol) in methanol (100 mL). After an exothermic reaction subsided the solution was heated at reflux for 2 h, and cooled to give a colorless precipitate that was isolated and recrystallized from hot methanol to give the indazolone **38**, 23.2 g (62%), mp 214–215°C; H NMR (DMSO-d_6): δ 2.70 (q, 4 H, CH_2), 7.13–7.63 (m, 4 H, aromatic); EI-MS: 186 (M^+). Anal. calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.03. Found: C, 70.70; H, 5.46; N, 15.14.

*1*H*-Benz[*g*]indazol-3-ol* **40**

A sample of palladium (10% on charcoal) was added to a solution of the indazolone **38** in 1,2-dichlorobenzene (5 mL). The mixture was heated at reflux for 2 days as the reaction was monitored with thin-layer chromatography (dichloromethane). The catalyst was isolated, the solvent was removed, and an ivory solid residue was recrystallized from isopropanol to give the benzindazole **40**, 0.39 g (78%), mp 245–247°C (dec.); H NMR (DMSO-d_6): δ 3.70. Anal. calcd for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found: C, 71.58; H, 4.40; N, 14.83.

*3a-Chloro-2,3a,4,5-tetrahydro-3*H*-benz[*g*]indazol-3-one* **39**

Chlorine gas was slowly passed into a suspension of the indazolone **38** (20.0 g, 0.1 mol) in dichloromethane (250 mL) as the solid gradually dissolved. The yellow solution was stirred for 30 min and the solvent was removed to give a solid that recrystallized from a mixture of benzene and petroleum ether to give the chloroindazolone **39**, 17.6 g (74%), 200–205°C (dec); H NMR ($CDCl_3$-DMSO-d_6): δ 2.30 (m, 2 H, CH_2), 3.10 (m, 2 H, CH_2), 7.20–7.90 (m, 4 H, aromatic, 11.72 (s, 1 H, NH). Anal. calcd for $C_{11}H_9N_2OCl$: C, 59.88; H, 4.11; N, 12.70; Cl, 16.33. Found: C, 59.62; H, 4.08; N, 12.45; Cl, 16.07.

*5,6,10,11-Tetrahydro-7*H*,9*H*-benz[6,7]indazolo [1,2-*a*]benz[*g*]indazol-7,9-dione* **35**

Potassium carbonate sesquihydrate (22.0 g, 0.13 mol) was added in one portion to a solution of the chloroindazolone **39** (11.0 g, 0.05 mol) in dichloromethane (100 mL). The mixture was stirred at room temperature as the reaction was monitored with thin-layer chromatography (dichloromethane). After the reaction was completed (16 h) the mixture was chromatographed (silica gel column, dichloromethane) to give an orange solid that was purified from a mixture of isopropanol and acetonitrile as the bimane **35**, 4.5 g (53%), mp 265–267°C; H NMR (($CDCl_3$): δ 2.58 (t, 4 H, CH_2), 2.99 (t, 4 H, CH_2), 7.03–7.38 (m, 8 H, aromatic); UV (CH_3CN): λ (ε) 419 (3137); EI-MS: 340 (M^+). Anal. calcd for $C_{22}H_{16}N_2O_2$: C, 77.63; H, 4.74; N, 8.27%. Found: C, 77.66; H, 4.83; N, 8.28%.

syn-*(α-Naphtho)bimane* **36**

A sample of palladium (10% on charcoal) (0.1 g) was added to a solution of the bimane **35** (3.4 g, 0.01 mol) in 1,2-dichlorobenzene (10 mL). The mixture was heated at reflux temperature for 2 days as the reaction was monitored with thin-layer chromatography (dichloromethane). Removal of the catalyst and solvent left a red residue that was purified (reprecipitated) from a mixture of hexafloropropan-2-ol and methanol, as *syn*-(α-naphtho)bimane **36** as a yellow powder, 2.4 g (71%); mp 313–315°C; H NMR ($CDCl_3$): δ 7.30–7.90 (m); UV (CH_3CN): λ (ε) 460 (10,201); fluorescence (CH_2Cl_2): λ (Φ) 492 (0.1); EI-MS: 336 (M^+). Anal. calcd for $C_{22}H_{12}N_2O_2$: C, 78.56; H, 3.60; N, 8.33. Found: C, 78.35; H, 3.66; N, 8.10. In the absence of a crystalline form an x-ray crystallographic analysis for the bimane **36** was not determined.

Acknowledgments

Financial assistance was received from ONR, ARO, Naval Weapons Center (China Lake, CA), and the Louisiana Board of Regents (LEQSF-RD-B-06). T.G.P. wishes to thank Naval Ocean Systems Center Independent Research program for support.

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