Bimanes. **19.** Characteristics of the Molecular Structures of 1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxabimanes) Determined by X-ray Crystallography

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The molecular structures of a variety of 1,5-diazabicyclo[3.3.0]octadienediones (9,10-dioxabimanes), including three 9,10-dioxa-*syn*-bimanes, three 4,6-bridged 9,10-dioxa-*syn*-bimanes, and three 9,10-dioxa-*anti*-bimanes, as determined by x-ray crystallography, are analyzed and compared with respect to planarity, bond distances, bond angles and intermolecular packing. "Planarity" may be the resultant of two non-planar equilibrium forms, a conclusion based on the anisotropic thermal motion parameters of the central N-N bond. "Amide"-type conjugation (N-C=O) is important in all planar bimanes; peripheral conjugation (N-C=C-C=O) is more significant in planar *syn*-bimanes and decreased conjugation is evident in the bent bridged *syn*-bimanes. Weak C-H···O bonds contribute significantly to the crystal packing arrangements.

Introduction.

The discovery of a simple synthesis of both *syn-* and *anti*-1,5-diazabicyclo[3.3.0]octadienediones (*syn-* and *anti*-9,10-dioxabimanes, see formulas **1** and **2** below) made a variety of these 5:5 bicyclic systems available (2,3). The fascinating chemical (3,5,7), photophysical (6) and photochemical (8) properties of the 9,10-dioxabimanes, as well as the usefulness of certain 9,10-dioxabimane derivatives as labeling agents for proteins, cells and tissues (9-12), prompted the need for detailed study and characterization of the molecular structures. We now describe the structural properties of a number of 9,10-dioxabimanes, discuss their significance and examine the influence of various substituents on dioxabimane conformation. A preliminary report on some of the structures has been published (13).
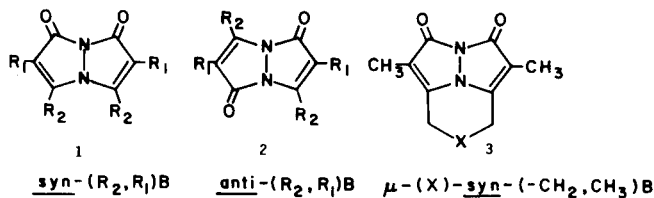
Results and Discussion.

The crystal structures of three representative compounds from each of three groups of 9,10-dioxabimanes (a total of nine compounds) were determined. In addition to *syn-* and *anti-* isomers with the same substituents as indicated by the general formulas **1** and **2**, a group of 4,6-bridged μ-(X)-*syn*-9,10-dioxabimanes **3** was studied. The syntheses of the compounds have been described elsewhere (3,5,7).

The formulas for the nine compounds which will be considered in the present article are presented in Scheme 1; each formula is accompanied by a description of the crystallographic site symmetry. Details concerning the solutions to the structural problems and their refinement have been presented in other publications (13-16).

The 1,5-diazabicyclo[3.3.0]octadienediones (briefly, the "bimanes") vary in the structural parameters from molecule to molecule over certain ranges which will be set forth in this section. A complete summary of bond distances, bond angles and dihedral angles appears in Tables 1 and 2. The labelling used for bond lengths and bond angles is given in Scheme 2.

Conformation and Flexibility.

The bimanes are flexible, cyclic conjugated systems, and the planarity of the molecules is the most important structural feature to be considered. The observed values for the ring-ring dihedral angle range from 180° to 139°. Only the simplest bimanes, *syn-* and *anti*-(CH₃,H)B and *syn-* and *anti*-(CH₃,CH₃)B, appear to be planar, an attribute independent of the crystallographic site symmetry. Bimanes with more complex substituents deviate significantly from planarity, *syn*-(C₆H₅,Cl)B being somewhat bent (dihedral angle = 172°), and *anti*-(C₆H₅,Cl)B more bent (147°). The three bridged compounds (**10** (139°), **11** (142°) and **12** (139°)) are all folded to the same degree, the stereochemistry being restricted by the geometry of the six-membered ring in a chair-like conformation. We illustrate the range of geometries open to the bimanes by juxtaposing the structures of *syn*-(CH₃,H)B and μ-(SO₂)-*syn*-(CH₂,CH₃)B (Figure 1A) and the structures of *anti*-(CH₃,H)B and *anti*-(C₆H₅,Cl)B (Figure 1B). The individual

Table 1

Bond Lengths and Averages (A) in Nine Representative Bimanes

	syn molecules			bridged molecules			anti molecules			all (d) molecules	Averages planar (d) molecules	bridged (d) molecules
	4	**5**	**6**	**10**	**11**	**12**	**7** (a)	**8**	**9**		**4, 5, 7, 8**	**10, 11, 12**
a	1.379	1.379	1.395	1.394	1.403	1.393	1.368	1.372	1.384	1.407	1.387 (13)	1.376 (6)	1.396 (6)
b	1.412	1.410	1.397	1.438	1.426	1.428	1.398	1.393	1.390	1.425	1.414 (15)	1.406 (12)	1.431 (5)
c	1.414	1.423	1.408	1.432			—	—		1.421			
d	1.385	1.361	1.376	1.405	1.395	1.403	1.380	1.374	1.387	1.399	1.385 (14)	1.376 (9)	1.402 (5)
e	1.372	1.372	1.373	1.407						1.393			
f	1.456	1.448	1.466	1.467	1.466	1.467	1.446	1.445	1.462	1.458	1.456 (11)	1.448 (9)	1.467 (1)
g	1.445	1.432	1.463	1.468						1.454			
h	1.350	1.375	1.356	1.337	1.353	1.343	1.337	1.338	1.333	1.353	1.351 (12)	1.350 (15)	1.344 (7)
i	1.358	1.361	1.363	1.343						1.365			
j	1.214	1.217	1.212	1.207	1.206	1.210	1.211	1.214	1.219	1.204	1.211 (6)	1.215 (5)	1.210 (5)
k	1.220	1.207	1.202	1.217						1.204			
l	—	1.478	1.699 (b)	1.489	1.491	1.491	— (c)	— (c)	1.496	1.693 (b)	1.490 (10) (c)	1.493	1.488 (6) (c)
m	—	1.506	1.685 (b)	1.479						1.698 (b)			
n	1.484	1.494	1.478	1.491	1.484	1.487	1.474	1.480	1.489	1.468	1.482 (9)	1.484 (6)	1.488 (3)
o	1.485	1.484	1.482	1.491						1.462			
Average esd:	(.003)	(.004)	(.007)	(.004)	(.003)	(.002)	(.003)		(.004)	(.004)			

(a) Two crystallographically independent half molecules in asymmetric unit. (b) C-Cl bonds. (c) For methyl substituents only. (d) e.s.d. of average in parentheses.

Table 2

Bond Angles and Averages (deg.) in Nine Representative Bimanes

	syn molecules			bridged molecules			anti molecules			all molecules	Averages planar molecules	bridged molecules
	4	**5**	**6**	**10**	**11**	**12**	**7** (a)	**8**	**9**		**4, 5, 7, 8**	**10, 11, 12**
a	109.7	109.5	110.7	107.7	107.2	108.2	109.8	109.6	109.4	108.5	109.1 (10)	109.6 (1)	107.6 (1)
b	109.6	109.5	110.4	107.4						108.9			
c	108.7	108.9	108.8	108.3	108.3	107.8	108.8	108.8	108.4	109.0	108.6 (4)	108.8 (2)	108.2 (2)
d	109.2	108.7	108.4	108.2						109.0			
e	140.7	141.0	138.1	127.9	129.1	127.5	141.4	141.6	142.2	130.0	134.3 (79)	141.6 (6)	125.4 (31)
f	142.1	142.3	141.2	121.4	123.8	123.1				129.8			
g	103.1	104.2	102.0	105.3	105.8	105.6	103.2	103.5	104.1	103.8	104.0 (12)	103.5 (4)	105.7 (3)
h	103.3	103.3	102.5	106.1						103.6			
i	132.6	131.7	132.7	130.6	130.5	130.3	133.0	133.0	132.2	130.5	131.8 (12)	132.7 (6)	130.6 (2)
j	132.9	133.7	132.9	130.8						130.9			
k	124.0	124.1	125.4	124.1	123.9	123.9	123.7	123.5	123.7	125.6	124.2 (8)	123.7 (4)	123.8 (4)
l	124.0	123.0	124.6	123.1						125.5			
m	—	123.1	121.4	122.2	122.8	123.0	—	—	122.3	120.7	122.0 (10)	122.4 (7)	122.7 (4)
n	—	121.7	122.1	122.9						120.1			
o	—	128.5	127.0	129.6	129.5	129.4	—	—	128.2	129.8	128.7 (10)	128.2 (3)	129.5 (1)
p	—	128.0	127.4	129.6						129.0			
q	110.0	108.4	111.4	108.2	107.7	107.6	110.4	110.1	109.5	110.8	109.8 (18)	109.9 (7)	107.8 (3)
r	110.5	110.3	110.3	107.5						110.9			
s	130.5	129.2	131.1	136.2	133.2	133.1	131.7	131.4	132.5	130.7	131.8 (20)	130.8 (11)	134.5 (16)
t	130.3	129.9	129.9	135.6						131.8			
u	121.4	121.7	121.8	113.5	116.5	116.2	120.4	120.7	118.8	121.3	119.5 (30)	121.0 (11)	115.0 (15)
v	121.8	121.9	122.0	114.0						120.7			
w	108.2	109.0	107.0	110.3	110.2	110.7	107.8	108.0	108.6	107.8	108.6 (12)	108.2 (5)	110.4 (2)
x	107.7	108.2	108.2	110.4						107.4			
Fold	180.0	180.0	171.6	139.3	141.8	138.9	180.0	180.0	180.0	147.3			
Average e.s.d.:	(0.2)	(0.2)	(0.4)	(0.3)	(0.2)	(0.2)	(0.2)		(0.2)	(0.3)			

(a) See footnote, Table 1.

five-membered rings are essentially planar in all the compounds except for the atoms at the 4- and 6-bridging positions in bimanes **10**, **11**, and **12**, for which there is a small deviation (< 0.1 Å) from the mean plane in a direction of the bridging groups.

The flexibility of the bimanes is reflected in the results of a thermal motion analysis for the atoms of the bimane structure; the mean square vibration amplitudes of the nitrogen atoms between the rings deserve particular attention. The values listed in Table 3 illustrate that the nitrogen vibrations are nearly isotropic in bridged bimanes **10**, **11**, and **12**, but are strongly anisotropic in the

Table 3

Thermal Vibration Amplitudes of the Nitrogen Atoms in Bimanes

Values of **1**, **m** and **n** represent vibration components along the three principle axes of inertia of the bicyclic framework of bimanes.

Planar Compounds	in Å^2		
	1	**m**	**n**
syn-(CH$_3$,H)B (a) (**4**)	0.025	0.021	0.049
	0.026	0.022	0.051
anti-(CH$_3$,H)B (b) (**7**)	0.034	0.032	0.087
	0.039	0.024	0.107
syn-(CH$_3$,CH$_3$)B (**5**)	0.035	0.043	0.142
	0.042	0.044	0.133
anti-(CH$_3$,CH$_3$)B (**8**)	0.051	0.043	0.118
	0.051	0.043	0.118
Bridged Compounds (c)			
μ-(C(CN)$_2$)-*syn*-(CH$_2$,CH$_3$)B (**10**)	0.042	0.033	0.045
	0.033	0.033	0.040
μ-(S)-*syn*-(CH$_2$,CH$_3$)B (**11**)	0.032	0.023	0.037
	0.024	0.023	0.027
μ-(SO$_2$)-*syn*-(CH$_2$CH$_3$)B (**12**)	0.028	0.027	0.037
	0.021	0.027	0.027

(a) Structure analysis carried out for crystal at -80°C. (b) Two crystallographically independent half-molecules in an asymmetric unit. (c) The second row of figures for each compound refers to the thermal parameters for the nitrogens which are part of the bridging ring.
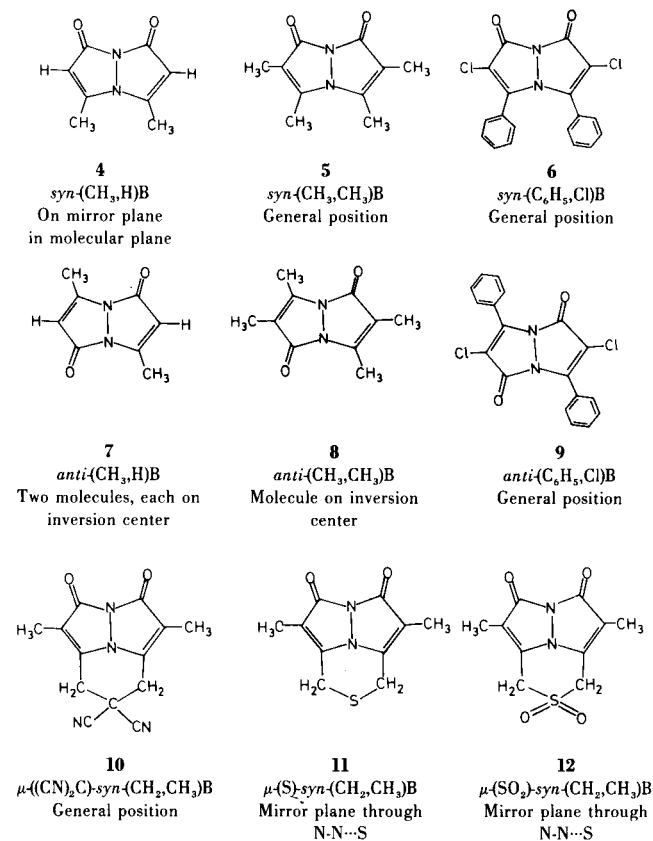
planar molecules **4**, **5**, **6**, and **7**. In the latter, the vibration tensor component of the nitrogen along the normal to the molecular plane is two to three times larger than the two other components in the molecular plane. It may be that the van der Waals radii of the central nitrogen atoms are smaller than those of the neighboring carbons, allowing those atoms more free space for a "genuine" vibration (17). However, the anisotropy of the thermal parameters for the nitrogens may also imply that the molecular structure is disordered in the solid and that the crystallographic results represent the average of (at least) two nonplanar equilibrium forms of the bimane molecule.

Obviously, none of the "unbridged"bimanes can be analyzed by using the rigid-body approximation of thermal motion. However, the 11-atom tricyclic framework of

the bridged bimanes is considerably less flexible in the solid. This is reflected in relatively small root-mean-square discrepancies between the observed and calculated thermal parameters, when the former are fitted to general rigid-body motions described by libration, translation and screw tensors (18): 0.0025 Å^2 (7.4%) for **10**, 0.0019 Å^2 (5.8%) for **11**, and 0.0017 Å^2 (5.3%) for **12**.

Scheme 1

Compounds Studied, Including Crystallographic Site Symmetry

4
syn-(CH$_3$,H)B
On mirror plane
in molecular plane

5
syn-(CH$_3$,CH$_3$)B
General position

6
syn-(C$_6$H$_5$,Cl)B
General position

7
anti-(CH$_3$,H)B
Two molecules, each on
inversion center

8
anti-(CH$_3$,CH$_3$)B
Molecule on inversion
center

9
anti-(C$_6$H$_5$,Cl)B
General position

10
μ-((CN)$_2$C)-*syn*-(CH$_2$,CH$_3$)B
General position

11
μ-(S)-*syn*-(CH$_2$,CH$_3$)B
Mirror plane through
N-N···S

12
μ-(SO$_2$)-*syn*-(CH$_2$,CH$_3$)B
Mirror plane through
N-N···S

It should be kept in mind that the bond lengths presented in Table 1 and discussed in the following section are not corrected for the effects of thermal motion. Corrections for librations in bridged molecules would be small (≤ 0.003 Å, largest amplitude of libration $= 3°$), while the influence of internal motions on the molecular geometry of the other bimanes is unclear, a point which will be discussed at the end of the paper. Furthermore, some chemically equivalent bond distances differ by as much as 0.010-0.015 Å, perhaps due to experimental errors of unknown origin; the distances have been averaged in such cases for consideration of their significance.

Intramolecular Distances and Conjugation.

There are five different bond types present in the molecular framework of the 9,10-dioxabimanes: C(sp^2)—C(sp^2),

$C(sp^2)=C(sp^2)$, $C(sp^2)=O$, $N(sp^x)—C(sp^2)$ and $N(sp^x)—N(sp^x)$, in which x = 2 in planar molecules and x > 2 in bent bimanes.

The nitrogen-nitrogen bond length (denoted as "a" in Scheme 2) varies from 1.370 Å to 1.407 Å. The shortest N—N distance is found in *anti*-(CH₃,H)B (7) (1.370 Å), the distances increasing in **4**, **5**, and **8** (1.378-1.384 Å), and **6**, **10**, and **12** (1.393-1.395 Å) to the longest N—N bonds in **11** (1.403 Å) and *anti*-(C₆H₅,Cl)B (9) (1.407 Å). The average value is 1.387 ± 0.13 Å, in excellent agreement with a representative N—N distance in an open chain compound like *N,N'*-diformylhydrazine, OCHNH—NHCHO (1.392 Å) (19). In fact, the N—N bond length in many 3-pyrazolin-5-one derivatives (13) clusters around an average between 1.39-1.40 Å (20-23).

13   14
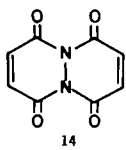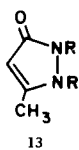
The greater the "fold" of the bimanes, the longer the N—N bonds, the longest bond being found in *anti*-(C₆H₅,Cl)B and corresponding to a bond order of 1.0 (24). The distances are thought to be affected by hybridization (nitrogens are conjugated and should have bonding radii to other atoms closer to sp² than sp³ particularly in planar molecules) and polarization (bond shortening in spite of positive charge on the nitrogens due to conjugation). The explanation is in accord with the model of Burke and Laing who showed that for a nitrogen involved in three sigma bonds rather than two, there will be a bond order increase (*i.e.*, a bond length decrease) due to delocalization of the lone pair electrons into the bonding system (25).

Characteristic distances for the N—C(=O) bonds "b" and "c" in Scheme 2) and the N—C(=C) bonds ("d" and "e" in Scheme 2) are slightly different. In most of the bimanes, the latter are invariably shorter than the former, reflecting a higher polarizability of the pi-electrons of a C=C bond as compared with those of a C=O bond.

The observed nitrogen-carbonyl bond lengths vary from 1.390 Å to 1.435 Å. (The results from the structural determination give slightly different values for the two equivalent bonds; the values have been averaged for consideration of the results.) Two *anti*-derivatives (**7** and **8**) show the minimum distance, 1.390 Å and 1.395 Å. The corresponding *syn*-bimanes, **4** and **5**, have appreciably longer bonds, 1.413-1.416 Å. The slightly bent *syn*-bimane *syn*-C₆H₅, Cl)B (**6**), has a N—CO distance of 1.402, whereas the distance in the corresponding *anti*-bimane is 1.428 Å, with the latter resembling the value in the bridged *syn*-bimanes (1.426 Å, 1.428 Å and 1.435 Å). A comparable range of N—CO bond lengths has been observed in the structure of 1,6-diazabicyclo[4.4.0]cyclodecadienedione

(14) with distances between 1.397 Å and 1.431 Å and a mean value of 1.42 Å (26).

The other nitrogen-carbon bond in the conjugated system, that between the nitrogen and the carbon-carbon double bond ("d" and "e" in Scheme 2), varies from 1.367 Å to 1.406 Å. Like the N—C(=O) bond lengths described above, the N—C(=C) bonds are shorter in the planar or almost planar bimanes (1.367-1.387 Å for **4-8**) than in the bent bimanes (1.395-1.406 Å for **9-12**). The difference might be ascribed to a lower degree of conjugation in the bent bimanes between the nitrogen non-bonding electrons and the other p-orbitals of the pi-system, and to a more sp³-like hybridization around the nitrogen.

The conjugation in the central part of the bimane molecules can be described in terms of the bond orders which can be derived for the N—N and N—C bonds, with reference to the correlations made by Burke and Laing (25). For N—N bonds, lengths between 1.370-1.407 Å correspond to bond orders between 1.20 and 1.05. Bond orders for N—C(=O) range from 1.25 to 1.05 and those for N—C(=C) between 1.30 to 1.15. The bond orders would be slightly smaller if the effect of thermal motion on the bond lengths were included. Thus, even in bent molecules, there is some delocalization of the nitrogen non-bonding electrons into the ring system. In the non-planar bicyclic molecule **14**, the N—N bond order is less than 1.0, while that of the N—C is close to 1.1 (26). The delocalization represents one mechanism for minimizing overlap between the non-bonding pairs. In parallel with the results obtained for **14**, the sum of the bond orders around the N atom in the bimanes is greater than 3.0, varying between the extremes of 3.1 in the least conjugated molecule, *anti*-(C₆H₅,Cl)B, to a maximum of 3.7 in the most conjugated molecule, *anti*-(CH₃,H)B.

The substantial variation in the carbon-carbon double bond distances, from 1.333 Å to 1.368 Å, suggests that bimane molecules are peripherally conjugated, with planar *syn*- compounds exhibiting more peripheral conjugation than the *anti*- isomers. Thus, the *anti*-bimanes, **7** and **8**, have the shortest C=C distances, 1.333 Å and 1.337 Å, characteristic of localized double bonds. The corresponding *syn*-bimanes (**4** and **5**) have the longest C=C distances, 1.354 Å and 1.368 Å, reflecting diminished double-bond character. Other C=C distances are between the extremes cited above.

The variation in the bond distances for the bond between the carbonyl and the carbon-carbon double bond ("f" and "g") is somewhat smaller than those already noted, from 1.440 Å to 1.467 Å, these being shorter than the characteristic C(sp²)—C(sp²) bond length in a quinone (27). However, the pattern of distance variation is not clearly correlated with the length of the adjacent C=C bond. The carbon-oxygen bond lengths ("i" and "k") show only a small variation in the bimanes examined, from

1.206 Å to 1.219 Å.

Folding the bimane molecule around the central N—N bond results in a considerable decrease in the value of the C—N—C angle ("f" in Scheme 2), from 142° in a planar structure to 121-124° in a bridged species. The latter is still more than 10° larger than the tetrahedral value, and must be accompanied by some conformational strain in the six-membered ring of the bridge. The strain is most apparent in the two CH_2—$C(CN)_2$ bonds in bridged bimane **10**, bonds which are appreciably longer (1.565 Å and 1.569 Å) than expected for a normal $C(sp^3)$—$C(sp^3)$ bond. The strain is less pronounced in the sulfur-bridged bimanes **11** and **12**, in which the geometry of the six-membered ring is very asymmetric (Bond lengths ca., 1.4 Å for C—N versus 1.8 Å for C—S, and bond angles of 124° for C—N—C versus 98-103° for C—S—C) (15).

Bond Angles.

In general, the average bond angles in bimane molecules are comparable to the analogous angles in pyrazolones (20-23). The internal angles within the five-membered rings may be considered to be derived from the ideal value of 108° expected for a regular planar pentagon and modified by the distortions of the ring from regularity. Thus, in the observed structures, the internal angle at the carbonyl carbon is consistently smaller by several degrees than the remaining angles of the ring, parallel to what is found for relating compounds like **14** (26).

Several bond angles of the bimanes change with the overall conformation of the molecules, their values being clearly associated with the foldedness of the bicyclic framework and the presence of the 4,6-bridging group. The compounds may thus be grouped according to the similarity of the angles; labels for the angles are given in Scheme 2.

Scheme 2

Labelling for Bond Lengths and Bond Angles
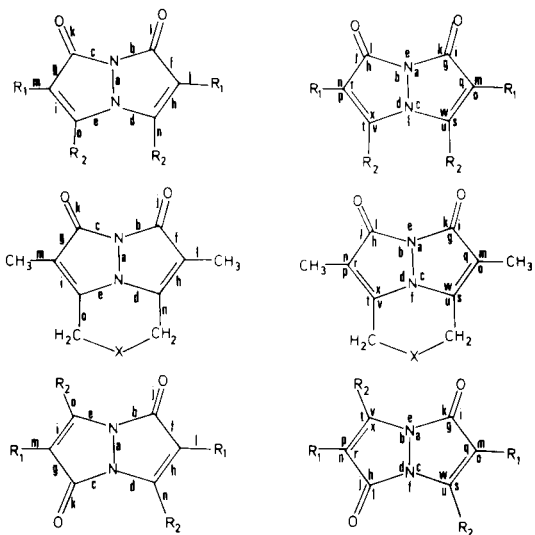
The internal angles of the pentacyclic ring around nitrogen ("a" and "b", "c" and "d") exhibit a fairly small range of values, from 107.2° to 110.6°. As an apparent result of increased delocalization of the nitrogen lone pair electrons into the carbonyl groups, the angles near the carbonyl in the planar species (average 109.8°) are slightly larger than those in the bridged syn-bimanes (average 107.6°). Correspondingly, the internal angles of the carbonyl group ("g" and "h") show the opposite trend, the smallest angle (102.3°) being that for a nearly planar syn-bimane (**6**) and the largest (105.7°) being those for the bridged syn-bimanes **10**, **11** and **12**. In turn, the external O=C—C angles ("i" and "j") are larger in the planar bimanes (132.7°) as compared with the bent bimanes (130.6°); these angles are uniformly larger than O=C—N angles ("k" and "l" average 124.2°), the latter being little influenced by structure. Further, the internal angles ("q" and "w", "r" and "x") (< C—C=C and < C=C—N) vary in a complementary manner between the planar and bridged bimanes, the sum for both being between 217.9° and 218.5°. The values of the internal angles in syn- and anti-$(C_6H_5,Cl)B$ are affected by the chlorine and deviate slightly from the trends described.

The external angles near nitrogen ("e" and "f") are very similar for all bimanes with small substituents (140.7°-142.3° for structures **4, 5, 7** and **8**). Within the syn-series, the angle on the carbonyl side is 1-3° smaller than its counterpart on the opposite side. The opposite order obtains in the bridged bimanes, < 4-5-6 ("f") (average 123°) being smaller by 4.5-6.5° than < 2-1-8 ("e") (average 128°). The strained tricyclic system has a further effect on the external angles around carbon atoms 4 and 6. (These atoms are displaced from the five-membered ring plane, as mentioned above). The C—C=C angles ("s" and "t") are considerably larger and the C—C—N angles ("u" and "v") significantly smaller in the bridged molecules than in the other bimanes (Table 2).

The deviation from the averages for the other angles is not particularly large, even for all nine bimanes considered together. For example, the "m" and "n" angles around carbons 3 and 7 are clearly less than the "o" and "p" angles, and independent of the nature of the R_1 group attached to the carbon. A similar relationship is found in the pyrazolones.

Intermolecular Arrangements.

The crystal structures of the bimanes exhibit a variety of packing modes and intermolecular interactions. The calculated densities range from 1.31 (**5**) to 1.40 gcm⁻³ (**4**) in light-atom compounds and from 1.45 (**11**) to 1.51 gcm⁻³ (**9**) in bimanes containing third-row elements such as sulfur or chlorine.
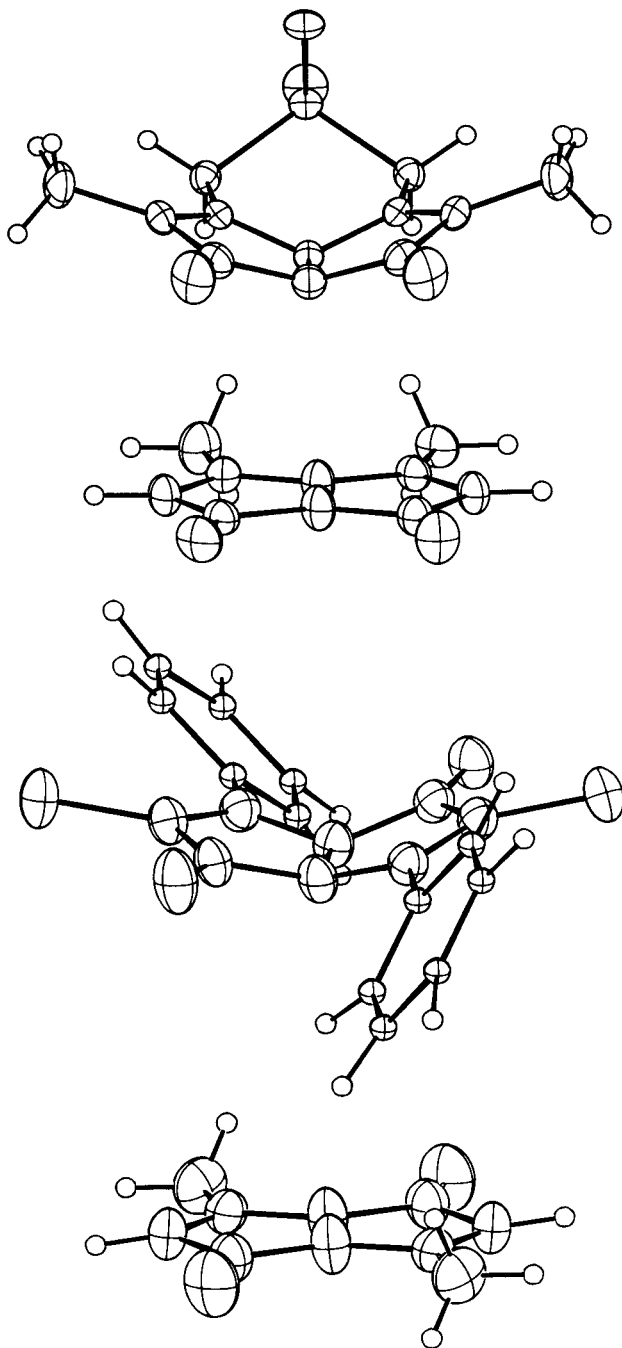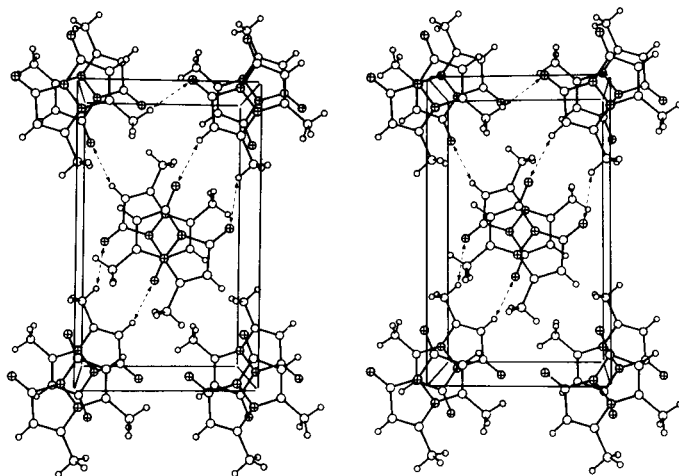
Figure 2. Stereoscopic packing diagram of *syn*-(CH₃,H)B (**4**) as viewed (approximately) down the stacking axis. (Space group *Pnma*, Z = 4; molecular planes coincide with the crystallographic mirror planes of symmetry). Several C-H···O interactions present in the structure are marked by dashed lines.

tacts (the shortest nonbonding distances are H···O = 2.4 Å and C···O = 3.34 Å). Molecules of adjacent layers alternate in orientation, almost entirely overlapping one another. The interlayer separation of 3.325 Å at room temperature is reduced to 3.273 Å for the crystal at −80°. (A phase transition occurs below that temperature.)

Short intermolecular contacts occur in the structure of *syn*-(C₆H₅,Cl)B which consists of pairs of opposed bimanes related by crystallographic centers of inversion (Figure 3). Each of the paired molecules is slightly bent around the N—N bond, the distance between the mean molecular planes being 3.32 Å and individual contacts ranging from 3.16 Å (shortest N···N contact) to 3.50 Å. The R₂ substituents for both *syn*-(C₆H₅,Cl)B and *syn*-(CH₃,H)B are outside of the region of overlap.

Figure 1. Overall views of the molecular structures of (a) planar *syn*-(CH₃,H)B (**4**) and bent μ-(SO₂)-*syn*-(CH₂,CH₃)B (**12**), (b) planar *anti*-(CH₃,H)B (**7**) and bent *anti*-(C₆H₅,Cl)B (**9**).

A most interesting packing arrangment is observed for *syn*-(CH₃,H)B for which the crystal consists of equally spaced molecular layers coinciding with the crystallographic mirror planes of symmetry (Figure 2) (16). Within the layers, there are relatively short CH···O van der Waals con-
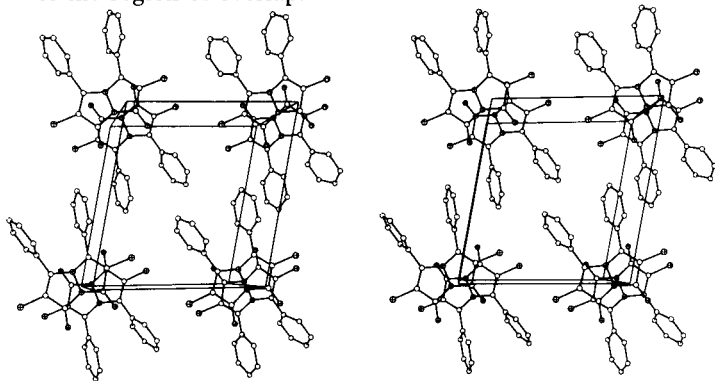

Figure 3. Stereoscopic projection of the crystal structure of *syn*-(C₆H₅,Cl)B (**6**), viewed along the normal to the mean molecular plane (Space group P1̄, Z = 2). Molecules are arranged in pairs across centers of inversion.

The arrangements and interplanar distances just mentioned are reminiscent of those found in pi-pi molecular complexes. Neither in the crystal nor in solution is there any evidence for charge-transfer absorption, and we therefore conclude that the pairing in the crystal is the result of dipole-dipole attractions with some contributions from crystal packing forces.

Somewhat surprisingly, one of the planar *syn*-bimane derivatives, *syn*-(CH$_3$,CH$_3$)B (**5**), crystallizes in a noncentrosymmetric space group P*c* with two molecules in the unit cell related to each other by glide symmetry (Figure 4) (14). Molecules are stacked along the shortest crystal axis, with a large interplanar separation of 3.65 Å, and avoid mutual overlap. The crystal structure is thus stabilized by repulsive interactions, with all molecular dipoles oriented in the same direction. Not surprisingly, the crystals have the lowest density (1.31 gcm^{-3}) of all the nine bimanes; moreover, the very substantial thermal motion of the central nitrogens in the direction normal to the molecular plane (Table 3) is consistent with a "loose" packing arrangement. We believe that the marked difference between the crystal structures of *syn*-(CH$_3$,H)B and *syn*-(CH$_3$,CH$_3$)B is related to the hindrance to close approach presented by the R$_1$ methyl groups at carbons 3 and 7.

Figure 5. Stereoscopic packing diagram of *anti*-(CH$_3$,H)B (**7**). (Space group P$\bar{1}$, Z = 2; the molecules are located on crystallographic centers of inversion) Several C-H⋯O contacts between adjacent columns in the structure are shown by dashed lines.

arises from extensive arrays of unique C—H⋯O bonds, the carbonyl oxygen acting as acceptor for the hydrogen donated by the carbon of the C=C double bond. The shortest non-bonding contacts present are C⋯O = 3.18-3.21 Å and H⋯O = 2.4 Å. The density and melting point differences between *anti*-(CH$_3$,H)B (d = 1.369
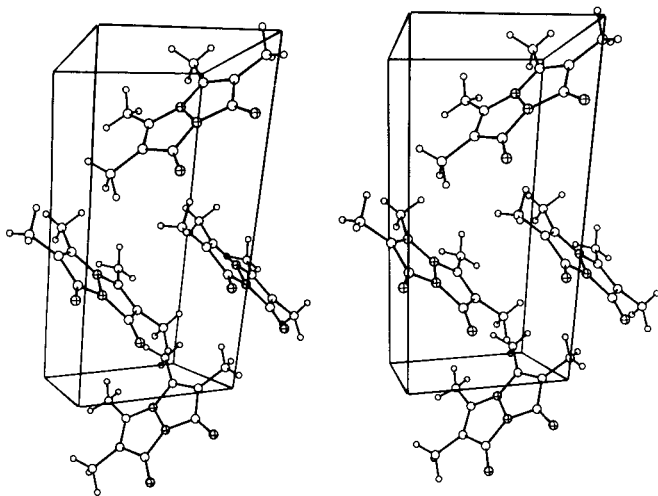

Figure 4. Stereoscopic projection of the crystal structure of *syn*-(CH$_3$,CH$_3$)B (**5**) viewed approximately down the shortest axis of the unit cell (Space group P*c*, Z = 2).

The three *anti*-isomers, **7**, **8** and **9**, crystallize in centrosymmetric structures, the simplest non-polar *anti*-(CH$_3$,-H)B and *anti*-(CH$_3$,CH$_3$)B being located on crystallographic centers of inversion (14,16). Almost all intermolecular distances in these structures are longer than or approximately equal to the sums of the appropriate van der Waals radii. However, as illustrated in Figure 5, intermolecular attraction in the crystals of *anti*-(CH$_3$,H)B also
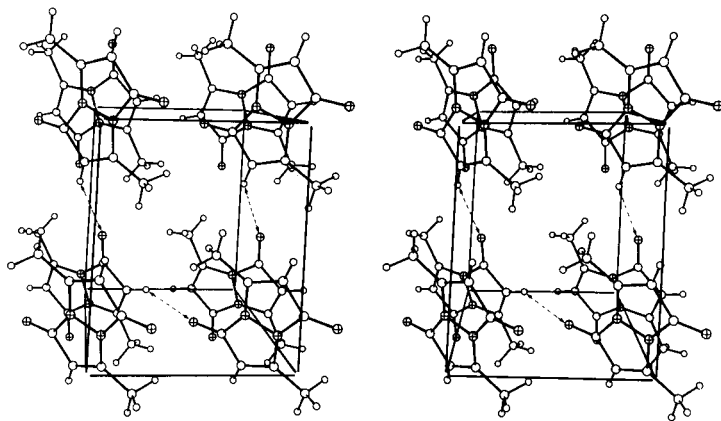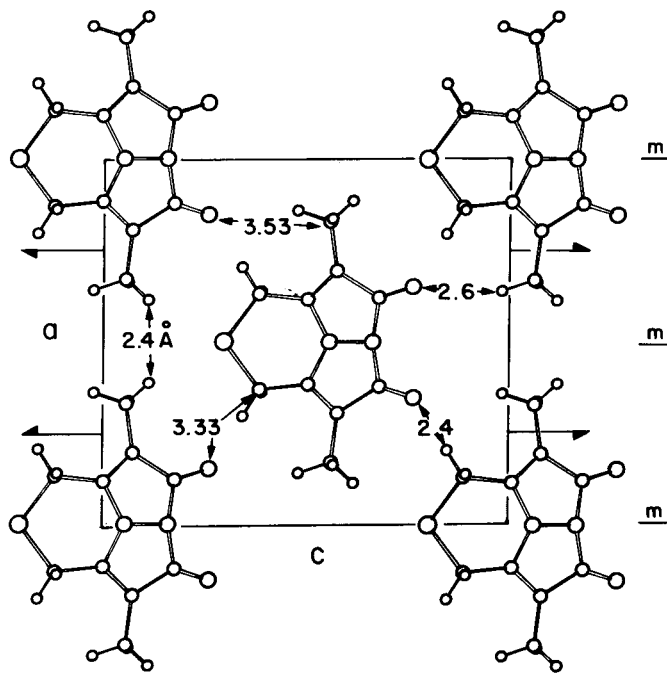

Figure 6. Crystal structure of μ-(S)-*syn*-(CH$_2$,CH$_3$)B (**11**) viewed down the **b** axis (Space group P*mn*2$_1$, Z = 2; symbols of some of the symmetry elements are marked on the figure). The shortest nonbonding intermolecular C-H⋯O contacts are shown.

gcm^{-3}, mp 178°) and *anti*-(CH$_3$,CH$_3$)B (d = 1.305 gcm^{-3}, mp 173°) reflect the contribution of these interactions to the stability of the crystal structure.

The packing arrangements of the three bridged *syn*-bimanes (**10, 11** and **12**) are also influenced to some extent by arrays of lateral C—H···O interactions. The carbons which donate the hydrogen are the methylene groups of the bridge, and the acceptors are either the carbonyl oxygens or the sulfone oxygen. The shortest nonbonding contacts include C···O(=C) = 3.33Å, C···O(=S) = 3.12Å, H···O(=C) = 2.4Å and H···O(=S) = 2.3Å. As a result of these interactions, the bridged bimanes form efficiently packed structures both in the centrosymmetric space groups (P2$_1$/c for **10** and *Pnma* for **12**) and the polar one (*Pmn2$_1$* for **11**). The packing arrangements for the compounds containing sulfur (**11** and **12**) are shown in Figures 6 and 7; that for **10** has been given elsewhere (16).

The crystal structure of μ-(SO$_2$)-*syn*-(CH$_2$,CH$_3$)B (**12**) is particularly complex as different types of specific interactions exist simultaneously. First, the structure, composed of layers perpendicular to the *a* axis, apparently optimizes
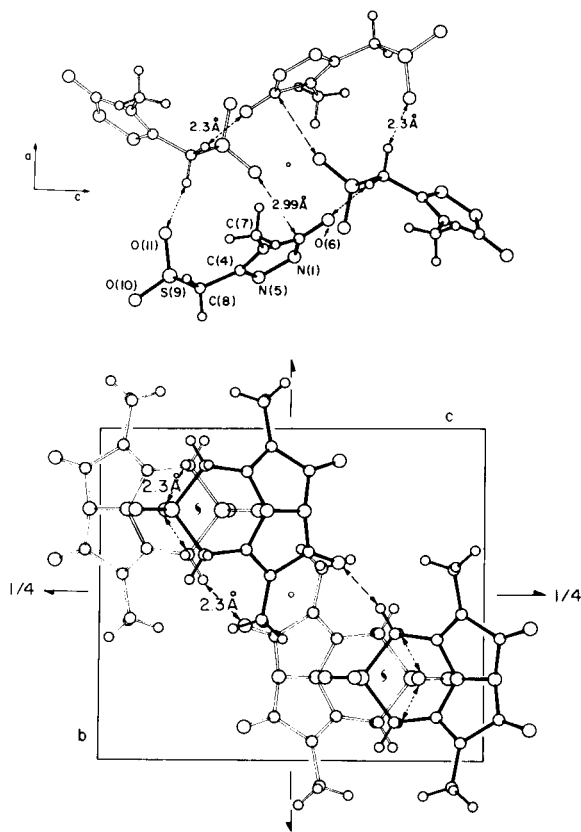
interactions between molecular dipoles with the polar groups of neighboring molecules oriented in opposite directions. Second, all four hydrogens of the CH$_2$ groups of the bridging group are involved in C—H···O interactions either with carbonyl groups within a molecular layer or with one of the sulfone oxygens between the layers. Third, a "pre-nucleophilic addition" interaction (28) between sulfone oxygen and the electrophilic carbon of a nearby carbonyl is present (Figure 7), the nonbonding O···C=O contact and approach angle being 2.99Å and 97°, respectively. Table 4 presents structural details on the lateral C—H···O interactions in the bimane crystals.

Conclusions.

Although the bimanes are flexible, their simple, symmetrical, cyclic conjugated systems might have led one to expect that the molecules might be planar. However, the non-bonding pairs which are formally associated with each nitrogen normally seek arrangements in which overlap is avoided, as in the case of cyclic hydrazines (29). Delocalization of the electrons into the carbonyl groups can certainly diminish the consequences of the tendency for the pairs to avoid one another, but delocalization (a) is limited by the amount of charge which builds up on adjacent nitrogens and (b) should be different for the *syn*-bimanes as compared with the *anti*-bimanes.

There are a number of planar bimanes. However, planarity is a structural feature which must be examined very carefully since the thermal parameters for the central nitrogens are considerably greater in the direction normal to the molecular plane than in the other directions. We

Figure 7. Two perspective views of the crystal structure of μ-(SO$_2$)-*syn*-(CH$_2$,CH$_3$)B (**12**) (Space group *Pnma*, Z = 4). (a) Projection on the crystallographic mirror plane (b) Projection on the mean molecular plane. The C-H···O and O···C=O interactions are marked by dashed lines.

Table 4

Geometric Parameters for C-H···O Interactions in Bimane Crystals (a,b)

(Bimane) Contact	C-H,Å.	C···O,A	H···O,A	C-H···O, deg	C···O=R, deg
(4)					
C(7)-H···O(9)=C	0.93	3.336	2.45	159	170
C(12)-H···O(10)=C	0.96	3.242	2.44	141	149
(7)					
C(3)-H···O(12)=C	0.95	3.209	2.40	142	169
C(9)-H···O(6)=C	0.92	3.182	2.37	147	177
(10)					
C(13)-H···O(9)=C	0.96	3.262	2.43	145	138
C(14)-H···O(10)=C	0.99	3.353	2.63	130	124
(11)					
C(8)-H···O(6)=C	0.96	3.329	2.42	157	147
(12)					
C(8)-H···O(11)=S	0.96	3.125	2.34	139	145
C(8)-H···O(6)=C	0.96	3.255	2.33	161	152

(a) Atom numbers given are those used in references 15 and 16. (b) In all cases, hydrogen atom positions were obtained directly from difference maps. No polarization effects were included, and therefore the actual H···O distances are probably somewhat smaller (≤ 0.1Å) than those listed.

Table 5

Rounded Distances (Å) and Angles (deg) (a)

Compound	Dihedral Angle (b)	OCNCO Angle (c)	N-N	OC-C=	C=C.	N-CO	N-C=	C=O
Averaged values for bimanes 4-12								
All bimanes	—	134	1.39	1.46	1.35	1.41	1.39	1.21
Planar bimanes	180	142	1.38	1.45	1.35 (d)	1.41	1.38	1.22
Bridged bimanes	140	125	1.40	1.47	1.34	1.43	1.40	1.21
Additional compounds (e)								
A (f)	180	141	1.38	1.46	1.34	1.41	1.36	1.21
B (g)	180	142 (c)	1.37	1.47	1.35	1.40	1.39	1.22
C (h)								
I	178	140	1.39	1.45	1.36	1.40	1.38	1.21
II	153	132	1.40	1.46	1.36	1.42	1.40	1.21
D (i)	161	137	1.39	1.45	1.35	1.42	1.38	1.22
E (j)	129	125	1.39	1.48	1.34	1.45	1.39	1.21

(a) Tables 1 and 2 list full crystallographic results. Full formulas are shown in Scheme 1. (b) the Angle between the planes of the two five-membered rings. (c) The external angle formed by =C-N-CO in *anti*-bimanes. (d) There is a distinct difference between the average value for the *syn*-compounds, 4 and 5 (1.36 Å) and the *anti*-compounds, 7 and 8 (1.34 Å). (e) Recent structures to be described in other contexts. (f) *syn*-(H,Cl)B. Synthesis: Bimanes 14. E. M. Kosower, D. Faust, M. Ben-Shoshan and I. Goldberg, *J. Org. Chem.*, **47**, 213 (1982). Crystal Structure: Bimanes **13**. I. Goldberg and E. M. Kosower, *J. Phys. Chem.*, **86**, 332 (1982); Spectroscopic properties: Bimanes **11**. E. M. Kosower, J. Hermolin, D. Faust and M. Ben-Shoshan, *J. Org. Chem.*, **46**, 4578 (1981). (g) *anti*-(HOCH₂,CH₃)B. Synthesis: *J. Org. Chem.*, **46**, 1666 (1981). Crystal structure to be described elsewhere. (h) Bis-*syn*-, *syn*-bimane derivative. E. M. Kosower, N. Gugoshinski and I. Goldberg, work in progress. The structure cited is interesting in that one bimane (I) is essentially planar, and one bimane (II) is bent. (i) *syn*-(COOCH₃,CH₃)B (Bimanes 14, *loc. cit.*). (j) μ-(−)-*syn*-(-CH₂,CH₃)B "zero-bridged" E. M. Kosower, J. Hermolin, B. Pazhenchevsky and I. Goldberg, work in progress.

may interpret these parameters as implying that the crystallographic structure represents the average of (at least) two non-planar forms. We have already alluded to this problem.

In addition to the implications of the thermal parameters derived form the crystallographic studies, the fact that in solution, the fluorescence emission spectra of "planar" *syn*- and bridged *syn*-bimanes are quite similar suggests that both have nonplanar emitting states (30). The equivalence of the hydrogens of the bridge methylene groups in nmr spectra (even at low temperatures) indicates a rapid interconversion between two equivalent forms of the type displayed in the crystal (5). On the other hand, the triplet state appears to be planar in its lowest energy state (attained at 2°K) on the basis of ODMR results for *anti*-(CH₃,H)-B (31). As a consequence of the proposition that the nonplanar forms are the equilibrium forms for all of the molecules, the carbon-nitrogen bond lengths in the "planar" bimanes should be increased by *ca.* 0.01 Å in order to represent more accurately the bond distances. The corrected distances are also appropriate for comparison with the corresponding distances in bimanes which are overtly non-planar in the crystal.

The available structural data strongly indicate that the conformation of bimanes around the N—N bond is mainly the result of intramolecular influences and is much less affected by intermolecular interactions. Thus, irrespective of the density of crystal packing, only the simplest bim-

anes appear to be planar; bimanes with more complex substituents are not planar. In fact, *anti*-(C₆H₅,Cl)B (9) is almost as bent in the crystal as the strained tricyclic 4,6-bridged *syn*-bimanes.

Changes in the overall conformation of the bimane moieties affect the hybridization of the nitrogen bonds, with considerable variation in the geometry of the molecule. Yet, certain geometric parameters are characteristic of the whole family of bimane molecules, with a relatively small spread of individual values around an average. The trends in the bond lengths and angles are seen in Table 5. Many geometric features are summarized, using values rounded off and averaged over all nine bimanes as well as presenting separate avarages for the planar and bridged groups of compounds. Structural data for several other bimane species (those most recently analyzed) are also included in this Table, confirming and extending the range of geometries illustrated in Figure 1 and indicated in Tables 1 and 2. Of particular interest in this context are the extremely strained "zero-bridged" bimane, μ-(−)-*syn*-(CH₂,CH₃)B, with the dihedral angle decreased to 129°, and the *syn*-*syn*-bis-bimane, in which one bimane is essentially planar and one bimane is bent.

We can make a number of statements about the values listed, judgements which are necessarily based on a relatively limited set of data. Nevertheless, the trends appear sufficiently clear to provide a basis for the following set of conclusions:

1. N—N—C=O conjugation is significant in all planar

or nearly planar bimanes, but is more important in *anti*-compounds than in *syn*-derivatives. The sum of the bond orders around the N atom is considerably greater than 3.0 (3.7 in *anti*-(CH$_3$,H)B).

2. Peripheral conjugation is present in *syn*-bimane molecules, increasing the C=C and slightly decreasing the N—C(=C) bond lengths (**5** *versus* **8**). In the *syn*-bimanes, the carbon-carbon double bond is about 0.02 Å longer than 1.34 Å, the normal value for a pentacyclic C=C bond.

3. The 4,6-bridged *syn*-bimanes as well as the *anti*-(C$_6$H$_5$,Cl)B derivative are rather bent around the N—N bond and therefore much less conjugated than the non-bridged compounds. In the extreme case of the "zero-bridged" bimane which has the least planarity of the molecules thus far examined, the lack of conjugation is reflected in further lengthening of the N—C and C—C bonds adjacent to carbonyl (Table 5).

4. Delocalized structural forms with charge separation seem much less important in bimanes than in monocyclic pyrazolones. Carbonyl bond lengths in pyrazolones are 1.24-1.27 Å (keto forms) (20-22) and 1.33-1.35 Å (enol forms) (20); carbonyl bond lengths in bimanes are close to those of localized bonds (1.21-1.22 Å).

There are several aspects of the present structural analysis which may be relevant to the functional properties of bimanes. The relatively small variation of the fundamental molecular structure in different environments is reflected in the relatively small difference between the hydroxide ion reactivities of similarly substituted *syn*- and *anti*-bimanes (32). The overall molecular conformation of the ground state has a significant effect on the light absorption of bimanes, *syn*-bimanes absorbing at much longer wavelengths than *anti*-bimanes. The bimanes appear to be useful as a semirigid support for potentially interacting groups at positions 4 and 6. A specific interaction between two carbomethoxy substituents has recently been observed (33).

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(4) 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 the 1,5-diazabicyclo[3.3.0]octadienediones has been thoroughly discussed in reference 3. The use of μ- as an abbreviation for the bridged compounds, for which an extensive description appears in reference 5, is done in analogy with the useage of μ- for bridged inorganic compounds. The usual abbreviations are illustrated under the formulas **1**, **2** and **3**.

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