d, $J = 2$ Hz, 2 × H-5), 7.32 (4 H, m, Ar H), 5.60 (1 H, d, $J = 1$ Hz, CHOEt), 3.60 (2 H, q, OCH$_2$Me), 1.24 (3 H, t, CH$_3$). Anal. Calcd for $C_{21}H_{14}Br_2O_5$: C, 49.83; H, 2.79. Found: C, 49.48; H, 3.10. The compound **6** (X = Br, R = Me) was similarly converted to **7** (X = Br, R = Me); mp 280 °C, in 75% yield by refluxing it in methanol in the presence of sulfuric acid; δ 8.30 (2 H, d, $J = 1$ Hz, 2 × H-2), 7.70 (2 H, d, $J = 2$ Hz, 2 × H-5), 7.28 (4 H, m, Ar H), 5.78 (1 H, d, $J = 1$ Hz, CHOMe), 3.60 (3 H, s, OCH$_3$). Anal. Calcd for $C_{20}H_{12}Br_2O_5$: C, 48.81; H, 2.46. Found: C, 48.50; H, 2.12.

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Registry No. **1a**, 17422-74-1; **1b**, 42059-81-4; **1c**, 42059-79-0; **1d**, 42248-31-7; **1e**, 52817-12-6; **1f**, 42059-80-3; **3a**, 491-38-3; **4d** (R = Me), 74729-96-7; **4e** (R = Me), 90368-62-0; **4f** (R = Me), 90368-63-1; **5a**, 52852-99-0; **5b**, 90368-64-2; **5c**, 90368-65-3; **6b** (R = Et), 90368-66-4; **6e** (R = Me), 90368-67-5; **6e** (R = Et), 90368-68-6; **7a** (R = Me), 90368-69-7; **7e** (R = Me), 90368-70-0; **7e** (R = Et), 90368-71-1; **8a**, 90368-72-2; **9a** ($R^1 = R^2$ = Me), 1776-08-5; triethylamine, 121-44-8.

Supplementary Material Available: Elemental analysis data for **4**–**6** (Table IIA–IVA) (3 pages). Ordering information is given on any current masthead page.

Bimanes. 20. Remarks on the Infrared Spectrum of 9,10-Dioxa-*syn*-(hydro,chloro)bimane (3,7-Dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione)

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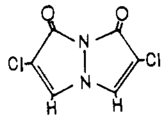
The bimanes are an interesting group of flexible bicyclic conjugated molecules.[2-9] Simple bimanes appear to be planar in the crystal. The crystal structure of *syn*-(H,Cl)B (**1**) [9,10-dioxa-*syn*-(hydro,chloro)bimane (3,7-dichloro-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione)] shows the molecules to be planar and tightly packed ($d = 1.863$ g cm^{-3}). However, high thermal parameters are found for the central nitrogens in the direction normal to the plane, and there are numerous bimanes with nonplanar structures in the crystal.[6,8] That bimanes equilibrate in solution between bent conformations is indicated by NMR spectra (averaging of different hydrogens on 4,6-bridging groups) and fluorescence spectra (bent and planar molecules have different absorption but similar emission spectra).[5]



1 *syn*-(H,Cl)B

Infrared spectra have been shown to be sensitive to intramolecular motion.[10] The effect of pressure (0–17 kbar) on the IR bands was studied to probe the influence of molecular motion within the crystalline environment of **1**. Restricting molecular motion of the bimane rings in the crystal should change the bands. It was also of interest to determine if pressure would induce a change in crystal structure.

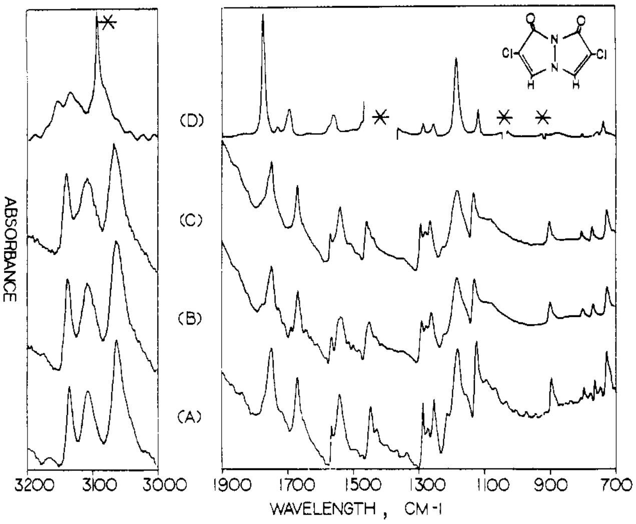


Figure 1. Infrared spectra of 9,10-dioxa-*syn*-(hydro,chloro)bimane [syn-(H,Cl)B] (**1**). Sample ground with KBr as pellet in a diamond anvil cell (DAC) at (A) 1 bar (atmospheric pressure), (B) 11 kbar, (C) 17 kbar or (D) as saturated solution [0.028 M] in CH$_3$CN [1900–1700-cm^{-1} region] (or in CD$_3$CN (1% CD$_2$HCN) [3200–3000-cm^{-1} region]). The solvent spectrum was subtracted from the measured spectrum to give the spectrum from which the frequencies were obtained. Starred (*) bands are partially (C–H region) or wholly solvent bands.

Previous work[2] had revealed an unexpected set of C–H stretching bands in the infrared spectrum of a crystalline thin film of **1**. In place of, at most, two bands (a symmetric and an antisymmetric stretch), three main bands are observed, and at least two additional bands are resolvable by curve fitting. This prompted us to investigate the origin of the extra bands, using a comparison of solution spectra with those of the solid phase, to assess the contribution of interactions within the crystal.

Results

The three bands found previously in the crystalline thin film for the C–H stretching region are also found for **1** in a KBr pellet (Figure 1). (One or two additional small bands are resolvable by Lorentzian curve fitting.) The band positions are at 3135, 3107, and 3063 cm^{-1}. The unusually sharp and strong band at 3160 cm^{-1} found in the crystalline thin film is absent. Pressure has only a small effect on the C–H bands, the absorption at 3135 cm^{-1} shifting to 3138 cm^{-1} (11 kbar) or 3139 cm^{-1} (17 kbar). The other bands hardly change, except for a slight broadening.

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Table I. Spectroscopic Data for 9,10-Dioxa-*syn*-(hydro,chloro)bimane [*syn*-(H,Cl)B]

CH_3CN solution[a]	solid		
	1 bar[b]	11 kbar	17 kbar
3154.3[a]	*c*	*c*	*c*
3135.1	3135.1	3138.3	3139.4
d	3107.3	3108.3	3107.6
d	3063.3	3063.6	3067.1
1774.9	1749.0	1748.4	1750.4
1730.7	*e*	*e*	*e*
1695.7	1670.9	1669.1	1669.7
1577.2	1567.3	1567.7	1569.3
1560.8	1541.9	1537.1	1538.9
1442.7	1447.7	1452.2	1458.2
1422.0	1428.9	*e*	*e*
1287.3	1289.3	1293.0	1295.1
f	1273.3	1276.9	1280.7
1255.7	1254.4	1262.6	1264.6
f	1213.7	1221.3	1227.0
1186.7	1181.6	1184.6	1182.1
1119.6	1125.8	1131.7	1133.7
f	897.0	900.9	903.7
801.5	798.3	802.4	804.7
756.4	764.6	770.1	773.7
737.9	728.7	728.9	728.1

[a] Obtained for a solution in CD_3CN (1% CD_2HCN). [b] Atmospheric pressure. [c] Bands not present. [d] Bands in this region are partially obscured by solvent absorption. [e] Shoulders; frequencies uncertain. [f] Bands obscured by solvent absorption.

The $C{=}O$ (1749 cm^{-1}) and $C{=}C$ stretching bands do not change in position with pressure except for the band at 1448 cm^{-1} which shifts to 1458 cm^{-1} (17 kbar). One set of bending vibrations shows a modest change with pressure, the absorptions at 1254, 1126, and 897 cm^{-1} shifting to 1265, 1134, and 904 cm^{-1} (17 kbar), respectively.

The C–H bands for 1 in most solvents ($CDCl_3$, CH_3COCH_3, CH_2Cl_2) resemble those in the KBr pellet except for one band (3084–3090 cm^{-1}) which shifts from 3107 cm^{-1} in the crystal. In CH_3CN solution, on the other hand, there are bands at 3154, 3135, and around 3080 cm^{-1}. The $C{=}O$ band is found at 1779 ($CDCl_3$), 1778 (CH_3COCH_3), 1777 (CH_2Cl_2), and 1775 cm^{-1} (CH_3CN) in solution.

A set of infrared spectra for syn-(H,Cl)B (1) under pressures from 0 to 17 kbar in a KBr pellet are compared to the spectrum of 1 in CH_3CN solution in Figure 1, and the observed frequencies are summarized in Table I.

Conclusions

1. The similarity of the spectra of 1 in solution and in KBr pellet indicate that the complexity of the C–H region has an intramolecular, rather than an intermolecular origin. The extra bands are most likely due to resonance enhancement of a binary combination of ring modes, probably those at 1543 cm^{-1} (in solution, 1568–1565 cm^{-1}). A similar example of such a Fermi resonance involving $C{=}C$ stretching bands has been observed for benzene.[11]

2. The effect of pressure on the IR bands was to cause a small shift to higher frequencies, as expected for the increased intermolecular interaction.[12] No other changes were observed as the pressure was raised. This implies that the crystal is already very well packed (high density, crystal structure) and resistant to further change. Another bimane, syn-(CH_3,H)B, although susceptible to a phase transition on cooling from 300 to 183 K, does not exhibit any change, detectable by X-ray diffraction, under 45-kbar pressure in a diamond anvil cell.[8]

3. The shift of the $C{=}O$ band (solution, 1779 cm^{-1} → crystal, 1750 cm^{-1}) may be due to either (a) the intermolecular H-bond or (b) electrostatic repulsion due to the molecules in the layers below and above the absorbing molecule. It may be noted (Figure 1) that the $C{=}C$ bands approach the carbonyl band in intensity for the pellet spectra. The relative intensification of the $C{=}C$ stretching band absorptions for the crystal suggests that the hydrogen bonding $C{=}O{\cdots}H{-}C$ (positions 4 and 6 in the bimane ring) enhances the contribution of the $C{=}O$ resonance forms, $C^+{-}O^-$ and $C^+{-}C{=}C{-}O^-$.

4. Further investigation of bimanes with small numbers of C–H bonds is warranted.

5. Infrared measurements as a function of pressure using a diamond anvil cell are a convenient way to probe both intramolecular behavior and intermolecular interactions in the solid state with a single set of measurements.

Experimental Section

Samples of *syn*-(H,Cl)B[9] (1) were examined with an evacuable Nicolet Model 8000 FTIR spectrometer equipped with a cooled MCT/InSb infrared detector. All spectra were recorded with a resolution of 2 cm^{-1}.

The spectra of the solids (pellets of crystalline 1 ground together with KBr) at various pressures were taken in a diamond anvil cell.[13] Pressures were established by evaluating the pressure-induced fluorescence shifts of ruby dust included in the KBr pellet.[14] At each pressure, the KBr pellet was annealed at 85 °C (a temperature previously found to be sufficient for 1) for several hours to ensure equilibration of the system. The spectra were the same before and after annealing. The spectra were resolved into Lorentzian curves by using the Nicolet curve analysis program.

Spectra of the solutions were somewhat difficult to obtain because of the low solubility of 1 (0.028 M in CH_3CN) in CH_3CN, $CDCl_3$, CH_2Cl_2, and CH_3COCH_3. Solvent bands were subtracted from the spectra of solutions of 1 by using a Nicolet subtraction routine.

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Registry No. 1, 78763-68-5.

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Reductive Amination of Ethyl 2-Oxo-4-phenylbutanoate with L-Alanyl-L-proline. Synthesis of Enalapril Maleate

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Inhibition of angiotensin-converting enzyme (EC 3.4.15.1) has been demonstrated to be an effective means

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