a razor blade to remove the semicrystalline resin deposits (112 mg). The scrapings were allowed to stand in 10 mL 1:1 dichloromethane/acetone for 2 h. The suspension was filtered and the filtrate reduced to ca. 0.5 mL under vacuum. TLC examination (silica gel; acetic acid/ethyl acetate, 1:99) showed 1 to be the major component.

A portion of this solution was evaporated to dryness (62 mg), dissolved in 5 mL ether containing a few drops of methanol, and esterified with diazomethane as above. Examination of this reaction mixture by TLC (silica gel developed with ether and with 1:1 dichloromethane/ethyl acetate; aluminum oxided developed with the same two solvent systems) showed 2 to be the major component. The ^1H NMR spectrum (60 MHz) of this mixture exhibited all the signals reported above for 2 in addition to those (principally in the δ 1–2 region) presumably ascribable to other uncharacterized constituents.

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Bimanes. 11. Random to Organized Rearrangements in Thin Films of *syn*-1,5-Diazabicyclo[3.3.0]octadienediones (9,10-Dioxa-*syn*-bimanes) Followed by Ultraviolet and Infrared Spectroscopy

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The facile synthesis, some crystal structures, and the interesting photophysical properties of the *syn*- and *anti*-9,10-dioxabimanes (1,5-diazabicyclo[3.3.0]octadienediones) have been reported.[2-7] A thin-film spectroscopy apparatus for distillable materials[8] allowed us to investigate a number of 9,10-dioxa-*syn*-bimanes. We can now report that the spectra of thin films of *syn*-(hydrogen,chloro)bimane (1) "plated" on an optical sapphire window at 77 K resemble those taken in CH_3CN (UV-vis) or $CHCl_3$ (IR) solution and that annealing the films leads to dramatic spectroscopic changes (UV-vis, IR, fluorescence) which appear to arise from the formation of ordered (crystallike) solids from random (liquidlike) glasses.

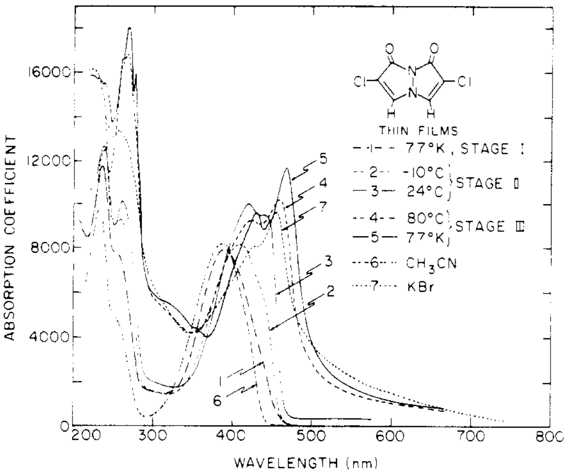
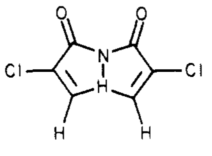
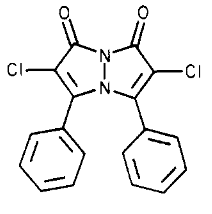


Figure 1. Spectra of 9,10-dioxa-*syn*-(hydrogen,chloro)bimane [*syn*-(H,Cl)B] in pure thin films, in a KBr window, and in CH_3CN solution. The bimane is distilled onto a sapphire optical window maintained at 77 K, producing a glassy (random) film (stage I; see curve 1). The similarity of the spectrum to that of the bimane in CH_3CN (curve 6) is evident. Annealing the film by warming it to between −10 and +24 °C leads to a shift in the longest wavelength absorption maxima (curves 2 and 3) to 416 and 440 nm and the change of a shoulder at 250 nm into an absorption band at 254 nm. Further annealing at temperatures between 75 and 85 °C leads to an additional shift of the long-wavelength maxima to 458 and 425 nm (curve 4), with a change to 468 and 430 nm (curve 5) on cooling to 77 K (stage III). The maximum at 254 nm becomes stronger and sharper in stage III. The spectrum of crystalline *syn*-(H,Cl)B dispersed in a KBr matrix resembles very much the spectrum of the stage III thin film (curve 7).



1 (*syn*-H,Cl)B)



2 (*syn*-(C_6H_5,Cl)B)

Plating [distillation at 155 °C (10^{-6} torr), condensation at 77 K] of *syn*-(H,Cl)B (1) (syntheses will be described elsewhere)[9] gave a thin film of bimane which exhibited the following spectroscopic characteristics: UV-vis λ_{max} 389 nm (ϵ 8100); fluorescence λ_{max} 485 nm ("normal" shape); IR 3135 (s), 3110, 3065 (C—H stretch), 1760, 1675, 1760/1675 cm^{-1} (intensity ratio ca. 10; C=O region). On annealing,[10] the spectra change strikingly in two distinct stages (initially stage I, succeeded by stages II and III).

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(8) Hermolin, J.; Levin, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1981**, *103*, 4801. A sapphire window (cooled to 77 K) is used to trap a jet of the material (e.g., pyridinyl radicals) under study. The amount deposited is measured interferometrically. The thin-film spectroscopy apparatus is small and may be easily transferred from instrument to instrument.

(9) Part 14: Kosower, E. M.; Faust, D.; Ben-Shoshan, M.; Goldberg, I., *J. Org. Chem.*, in press. The new bimane, *syn*-(H,Cl)B, had spectroscopic properties (UV, IR, NMR, mass) consistent with the assigned structure and gave a satisfactory elemental analysis.

(10) The film is warmed to a specified temperature and then cooled to 77 K. Spectra measured under these conditions are generally sharper. Cooling is particularly important in the case of the IR spectra since measurement of the spectra at scan speeds low enough to give well-defined spectra may be accompanied by IR heating of the sample and thus further annealing.

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

state	UV-vis,[a] λ_{max}, nm	IR, ν_{max}, cm^{-1}	fluorescence,[b] λ_{max}, nm (ϕ_F)
stage I[c]	389	3135 (s), 3110, 3065, 1760, 1675	485
stage II[d]	416	3142, 3110, 3065, 1755, 1672	492 (br)
stage III[e]	458 (468)[f]	3160, 3110, 3065, 1750, 1665	492 (496[g])
CH_3CN[h]	388		443 (0.40)
KBr[i]	457	3140, 3110, 3060, 1740, 1675	ca. 495
7930[j]	390		462
CH_3OH[k]	386		
$CHCl_3$[l]		3100 (vbr), 1780, 1700	

[a] Changes in the 210-270-nm region are not listed (see Figure 1). [b] Excitation were similar to absorption maxima in all cases. [c] Glassy (random) film deposited on sapphire window at 77 K. Thickness: UV-vis, ca. 0.2 μm; IR, ca. 2.0 μm. [d] Random film (footnote *a*) annealed at −10 to +15 °C. [e] Random film (footnote *a*) annealed at 75-85 °C. [f] Cooled to 77 K; a second band at 430 nm is also present. [g] Cooled to 77 K; shoulder at 530 nm. [h] *Z* value (solvent polarity parameter) is 71.3 (cf. Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253). [i] Carefully pressed pellet. [j] Corning porous glass. A film deposited at a nominal temperature of 77 K was annealed at 90 °C to obtain the result noted in the table. Given the reported surface area for the glass and the quantity deposited on the surface, the film which was examined must have been very thin, since the average pore diameter in the glass is 40 Å. [k] Methanol, *Z* = 83.6 (see footnote *h*). [l] Chloroform, *Z* = 63.2 (see footnote *h*).

In the UV-vis region, the absorption maximum shifts from 389 to about 416 nm with a second band at 440 nm (stage II) when the sample is warmed to no more than about 25 °C, but the intensity changes relatively little. At higher temperatures (75-85 °C), the maximum shifts further to 458 nm with a second band at 425 nm (at 77 K, 468 and 430 nm; stage III). The fluorescence spectrum at stage II changes to a flat-topped broad band reminiscent of those for crystalline powders, with a broad maximum at 492 nm. At stage III, the fluorescence spectrum narrows again, with a maximum at 492 nm.

The IR spectrum in both the C—H and C=O stretch regions changes appearance on annealing. Narrow bands replace broad bands at stage II and change further at stage III, with an especially sharp band appearing at 3160 cm^{-1} and the 1760/1675-cm^{-1} ratio falling to about 3. Material recovered from the optical window is shown to be absolutely pure *syn*-(H,Cl)B in the expected amount.

The spectroscopic shifts observed for the thin film of *syn*-(H,Cl)B are in contrast with the minimal effect of solvent polarity changes on the position of the UV-vis maximum, as illustrated in Table I. The geometry of the molecules in solution is no doubt different from that of the molecules in the crystal[11] but similar to that in the glassy state. UV-vis spectra found for *syn*-(H,Cl)B in stages I-III as well as in KBr and in solution are shown in Figure 1. IR spectra are given in Figure 2. Parallel spectroscopic results in thin films, in a KBr matrix, and in solution were obtained for *syn*-(C_6H_5,Cl)B (2).

The spectroscopic changes in all regions are interpreted as the result of changes in the physical arrangement of the molecules in the thin film. On annealing, the initial random (glassy) arrangement of the molecules in stage I is replaced in stage II by an arrangement of limited order in which the molecules are planar, the latter then giving rise to the greater order of the crystal in stage III. Crystal structure studies of bimanes[3,12,13] have shown that many of the *syn*-bimanes are planar or close to planar in the crystal. Repeating sequences of pairs of oppositely directed (apposed antiparallel) molecules are often present, the intermolecular distance being about 3.1 Å. The crystal structure of *syn*-(H,Cl)B exhibits a stacked, alternating, antiparallel arrangement with an intermolecular distance of 3.4 Å.[14] No charge-transfer band appears in the spectra of the thin films, and electrostatic forces appear to be responsible for the packing. The stage I to stage II shift in the UV-vis maximum is due to the change from bent to planar molecules. Dipole–dipole interactions between the S_1 excited-state molecules and neighboring S_0 molecules account for the major spectroscopic shift in the maximum seen in stage III as compared with that in stage II. The calculated Davydov splitting is too small to account for the major spectroscopic shift but can explain the shoulders on the main bands. Detailed discussion will

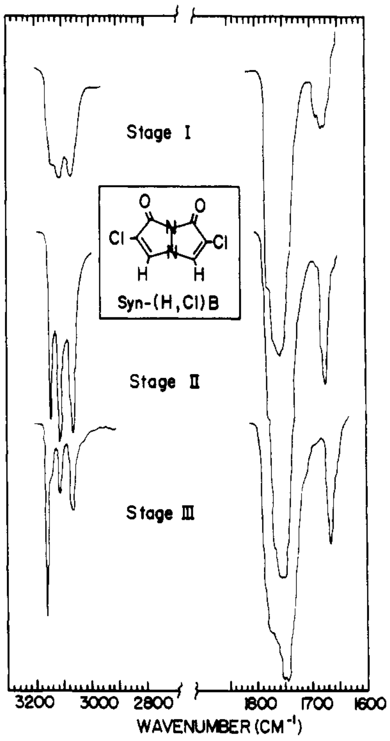

Figure 2. Infrared spectra of 9,10-dioxa-*syn*-(hydrogen,chloro)bimane (*syn*-(H,Cl)B, 1) in thin films. The stage I film (random, glassy) was deposited on a sapphire window at 77 K and annealed to produce a stage II film (−10 to +24 °C) and then a stage III film (75–85 °C). Observation of the spectrum is limited by the infrared absorption of the sapphire window (cutoff at ca. 1620 cm^{-1}). No other absorption bands were present in the spectrum.

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(13) Bernstein, J.; Goldstein, E.; Goldberg, I. *Cryst. Struct. Commun.* **1980**, *9*, 295, 301.

(14) The X-ray crystal structure of *syn*-(H,Cl)B and its relationship to the spectroscopic changes observed on annealing the crystal will be discussed separately. Goldberg, I.; Kosower, E. M., submitted for publication.

appear in connection with a report of the crystal structure of *syn*-(H,Cl)B.[14] The unusually strong C–H stretching vibration which appears in the stage III IR spectrum is probably due to intermolecular hydrogen bonding, with a C—H···O=C bond between bimanes in the same plane.[14]

It is interesting to note that Seki and Itoh[15] have proposed that rearrangement of anthracene in ultrathin films from random order to "dimers" is responsible for the spectroscopic shifts in the UV–vis spectra appearing after annealation over the range from 6 to 240 K. We have created "ultrathin" films of *syn*-(H,Cl)B on Corning glass 7930; such films show UV–vis absorption spectra like those obtained for glassy films or solutions.[16]

The orange color of *syn*-(H,Cl)B crystals is clearly deeper than might have been expected from the light yellow solutions of the compound. The present results demonstrate that the spectroscopic properties of the crystal are different from those of the molecules in solution and that modification of the electronic transitions of the molecule rather than new absorption due to complex formation is involved.

In summary, we have shown that solid-state spectroscopic properties of the *syn*-bimanes are easily studied and have a variety of interesting features. Both kinetic and equilibrium changes should be accessible to study. The apparatus we use is convenient and simple compared to the usual ones for thin films.[15] Its use opens the field of physical and chemical investigation on thin films of organic materials in glassy and crystalline states to those without elaborate cryoscopic equipment.

Acknowledgment. We are grateful to the European Research Office, United States Army, for support.

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[16] The special experimental conditions required for deposition of material on optical windows of Corning glass 7930 ("thirsty glass") are as follows: A copper ring is used to attach the 7930 optical window to the inner liquid N$_2$-cooled sapphire window of the thin-film spectroscopic apparatus (see ref 8). Deposition is carried out slowly, but the spectra observed are characteristic of stage II organization. However, annealing at ca. 90 °C produces a film with a stage I spectrum, indicating that the *syn*-(H,Cl)B had penetrated the pores of the porous glass and formed a thin film. Whether the stage I spectrum is simply the result of the diminished intermolecular interaction (like that in a glassy film) in an ultrathin film and the consequent lack of long-range organization or the result of interaction of the *syn*-(H,Cl)B in a moderately organized state (local groups of no more than five to seven molecules could be stacked in the 40-Å-diameter pores) with the surface of the 7930 glass cannot now be ascertained.

Direct (One Pot) Synthesis of Organoselenium and Organotellurium Compounds from the Metals[1]

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The chemistry of organoselenium compounds has been growing in recent years, because of the many synthetic applications of organoselenium compounds.[2]

Table I. Photostimulated Reaction of Iodobenzene with Selenide and Telluride Ions in Liquid Ammonia^{a}

PhI, mmol	XNa$_2$,^{b} mmol	method^{c}	product^{m} (yield, %)
		For X = Se	
9.96	4.97	A	PhSePh (12),^{d} PhSeSePh (78)^{d}
9.87	4.94	B	
9.96	4.98	C,^{e} A	PhSeSePh (76)^{f}
17.10	8.55	C, A	PhSeSePh (92)^{f}
10.14	5.06	C, D	PhSeMe (67)^{g}
9.90	4.95	C, E	(1-Naph)SePh (67),^{d} PhSeSePh (29)^{d}
10.14	5.07	C, F	(1-Naph)SePh (98)^{f}
9.99^{h}	5.00	C, D	(o-MeC$_6$H$_4$)SeMe (87)^{f}
		For X = Te	
10.76	5.29	A	PhTePh (17),^{i} PhTeTePh (17)^{i}
9.96	4.99	B	
10.00	5.01	D	PhTePh (21),^{i} PhTeMe (29)^{i}
10.05^{j}	5.02	A	(1-Naph)$_2$Te (35),^{k} (1-Naph)$_2$Te$_2$ ^{l}

^{a} Reactions were carried out in 250–300 mL of dry liquid ammonia and were irradiated 4 h with four 250-W UV lamps (Philips, Model HPT, water refrigerated). ^{b} Prepared in situ by 1 mol of selenium or tellurium metals and 2 mol of sodium metal. ^{c} A, the reaction mixture was air oxidized: B, dark reaction; C, after the irradiation sodium metal was added until a blue solution was obtained; D, the reaction was quenched by methyl iodide; E, 1-iodonaphthalene (5.0 mmol) was added, and the reaction was irradiated for 50 min; F, 1-iodonaphthalene (5.1 mmol) was added, and the reaction was irradiated for 160 min. ^{d} Determined by GC with phenanthrene as an internal standard. ^{e} One-hour irradiation. ^{f} Isolated yield. ^{g} Isolated as the dibromide. ^{h} *o*-Iodotoluene. ^{i} Determined by GC with 9-bromophenanthrene as an internal standard. ^{j} 1-Iodonaphthalene. ^{k} Determined by GC with 9,10-dibromophenanthrene as an internal standard. ^{l} Not quantified. ^{m} Naph = naphthyl.

One convenient method for the synthesis of symmetrical and unsymmetrical diaryl selenides is the photostimulated reaction of phenyl selenide ion and aryl halides in liquid ammonia by the S$_{RN}$1 mechanism.[3,4]

We now describe the photostimulated reaction of iodobenzene with selenide ion as the nucleophile, which can be used as a "one pot" method to prepare arylselenols, diaryl diselenides, aryl alkyl selenides, and symmetrical and unsymmetrical diaryl selenides in excellent yields.

Results and Discussion

Selenide ion can be formed from the reaction of selenium and sodium metals in liquid ammonia (eq 1).[5]

$$\mathrm{Se} + 2\mathrm{Na} \xrightarrow{\mathrm{NH_3}} \mathrm{Se}^{2-} + 2\mathrm{Na}^{+} \qquad (1)$$

When a solution of selenide ion thus prepared and iodobenzene was irradiated and the resulting solution was air oxidized,[6] diphenyl selenide and diphenyl diselenide were obtained (Table I). In the dark there is no reaction, thus ruling out benzyne or other alternative mechanisms.

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[1] Research supported in part by the Consejo National de Investigaciones Cientificas y Técnicas and the Subsecretaria de Ciencia y Tecnologia, Argentina.

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