H-3, at δ 4.64 (br dd, *J* = 3.0, 1.5 Hz),[15] as the equatorial orientation, indicating the right stereochemistry for maytansinol (**2**).

Similarly, treatment of the epoxy aldehyde **20** with lithium enolate of EtOAc (5 equiv in THF, −78 °C, 30 min) now produced the adduct as almost all single isomer **27a** (Scheme IV). Its hydroxy group was protected with Me$_2$-*t*-BuSiCl [5 equiv and imidazole (12 equiv) in DMF, 35 °C, 12 h], and then the carboxylic ester **27b** was hydrolyzed with a mixture of 3 N 1:5:2 KOH–EtOH–THF (45 °C, 7 h) to **27c** (52% overall yield from **20**). Cyclization of the acid **27c** was achieved with mesitylenesulfonyl chloride[2b] (20 equiv *i*-Pr$_2$EtN (20 equiv and *n*-Bu$_4$NOH in benzene, 40 °C) to afford **28a** [^{1}H NMR δ 1.00 (Me-6, d, *J* = 7 Hz), 1.08 (Me-4), 1.96 (Me-14), 2.94 (H-5, d, *J* = 9 Hz), 3.72 (H-10, d, *J* = 8.5 Hz), 5.24 (H-13, d, *J* = 10 Hz), 5.40 (H-11, dd, *J* = 15, 8.5 Hz), 6.46 (H-12, dd, *J* = 15, 10 Hz), 6.56, 6.72 (Ar 2 H, s); *m/z* 795 (M+)] in 53% yield. Desilylation of **28a** was achieved with *n*-Bu$_4$NF (5 equiv) only in the presence of MeCN as solvent with THF (2:1), [60 °C, 12 h] to form the diol **28b** in 77% yield [*m/z* 567 (M+); IR ν 3500, 1642 cm^{-1}]. The hydrolysis of the dimethyl ketal **28b** with a mixture of 1:3:1 AcOH–THF–H$_2$O (35 °C, 11 h) to give in quantitative yield the ketone **29** [IR ν 1724, 1644 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.87 (Me-4), 1.16 (Me-6, d, *J* = 6.6 Hz), 2.55 (H-5, d, *J* = 9.5 Hz), 2.76 (H-8, dd, *J* = 17.5, 3.0 Hz), 6.81, 6.83 (Ar 2 H, d, *J* = 2 Hz); *m/z* 521 (M+)]. Treatment of the keto diol **29** with *p*-nitrophenyl chloroformate[16] [4 equiv with Py (4 equiv) in dry CH$_2$Cl$_2$, 0 °C 15 min] and then with NH$_3$ [in MeOH with cooling, 20 min] produced maytansinol (**2**) [^{1}H NMR (400 MHz) δ 0.84 (Me-4), 1.25 (H-8), 1.29 (Me-6, d, *J* = 6.5 Hz), 1.54 (H-6, m), 1.69 (Me-14), 2.10 (H-2, dd, *J* = 13.5, 2.0 Hz), 2.15 (H-8, d, *J* = 14.0 Hz), 2.28 (H-2, dd, *J* = 13.5, 11.0 Hz), 2.57 (H-5, d, *J* = 9.5 Hz), 3.11, 3.47 (2 H-15, d, *J* = 12.5 Hz), 3.20 (OMe-10), 3.35 (NMe), 3.49 (H-10, d, *J* = 9.0 Hz), 3.54 (H-3, dd, *J* = 11.0, 2.0 Hz), 3.98 (ArOMe), 4.34 (H-7, t, *J* = 11.0 Hz), 5.51 (H-11, dd, *J* = 15.0, 9.0 Hz), 6.14 (H-13, d, *J* = 11 Hz), 6.43 (H-12, dd, *J* = 15.0, 11.0 Hz), 6.80 (Ar H, d, *J* = 2 Hz), 6.98 (or 7.02)[17] (Ar H, d, *J* = 2 Hz)] in 67% overall yield. HPLC and TLC of (±)-maytansinol were also superimposable[17] with the authentic maytansinol.

We have now accomplished the total synthesis of (±)-maytansinol. The total synthesis of racemic maytansinol involves the solution of the crucial problem that all of the asymmetric centers were prepared ahead of 19-membered lactam ring closure, thus, that only one asymmetric center was present in the original starting material, acrolein dimer, and all other six asymmetric centers in **2** were *intramolecularly* induced in high stereospecificity. We have also finished the syntheses of (±)-maysine and (±)-*N*-methylmaysenine along this line.[13]

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Registry No. (±)-**2**, 57103-68-1; (±)-**3**, 77943-81-8; (±)-4, 77890-94-9; **5**, 82598-93-4; **6**, 82598-94-5; **7**, 82598-95-6; **8a**, 82614-13-9; **8b**, 82598-96-7; **9a**, 82598-97-8; **9b**, 82598-98-9; (±)-**10**, 82598-99-0; (±)-**11**, 82614-14-0; **12**, 82599-00-6; **13**, 82599-02-8; (*E*)-**14a**, 67705-17-3; (*Z*)-**14a**, 82599-21-1; (*E*)-**14b**, 67705-16-2; (*E*)-**14c**, 74510-49-9; (*E*)-**14d**, 82599-03-9; (*E*)-**15**, 82599-04-0; (±)-**16**, 82599-05-1; (±)-**17**, 82599-06-2; (±)-**18**, 82599-07-3; (±)-**19**, 82599-08-4; (±)-**20**, 82599-15-3; (±)-**21**, 82614-15-1; (±)-**22a**, 82599-09-5; (±)-3-*epi*-**22a**, 82637-92-1; (±)-**22b**, 82599-10-8; (±)-**23**, 82599-11-9; (±)-**24**, 82614-16-2; (±)-**25**, 82599-13-1; (±)-**26**, 82599-14-2; (±)-3-*epi*-**26**, 82659-78-7; (±)-**27a**, 82599-16-4; (±)-**27b**, 82599-17-5; (±)-**27c**, 82599-18-6; (±)-**28a**, 82614-17-3; (±)-**28b**, 82599-19-7; (±)-**29**, 82599-20-0; 4-bromo-2-pentene, 1809-26-3; sodium *p*-anisyoxide, 53942-86-2; 2-chloroethanol, 107-07-3; 4-lithio-4-(phenylsulfonyl)-1-pentene, 82599-01-7; ethyl acetate lithium salt, 56267-15-3; (±)-maysine, 72880-43-4; (±)-*N*-methylmaysenine, 67045-55-0; Ph$_3$P=CHOCH$_2$Ph, 82599-12-0.

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(15) The epitriacetate corresponding to **26** derived from 3-epi-**26** showed axial H-3 at δ 4.93 (dd, *J* = 10, 2.5 Hz) at 400 MHz.

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(17) In connection to the identification of maytansinol, it should be strongly noted that the signal corresponding to one of the two aromatic protons has been reported as δ 7.05 by Kupchan et al.[1b] and as δ 6.91 by Meyers et al.[2a] (no value reported in ref 2b). We found that this signal appeared at different chemical shifts depending upon the concentration of **2**: the higher in concentration, the lower in chemical shifts, while the other aromatic signal at δ 6.8 and other signals sparingly changed irrespective of the concentration.

Microwave Structure Determination for the Furan–HCl Complex

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The structure of the furan–HCl complex in the gas phase has been determined from measurements of rotational transition frequencies. Analysis of the data indicates a planar structure for the complex with an oxygen–chlorine distance of 3.27 (1) Å.

It is well-known that furan has a high probability of being protonated in acidic solutions. Molecular orbital calculations[1] and calorimetric studies[2] for furan–HX complexes have been carried out. Furan has a conjugated π-electron system and an oxygen atom, so complexes of this type should provide information on the relative importance of these properties for hydrogen-bond formation. Actual structure measurements on these complexes are helpful in evaluating the numerous molecular orbital calculations on hydrogen-bonded complexes.

The microwave rotational transitions were observed by using a pulsed-nozzle Fourier transform spectrometer developed by Balle, Flygare, and co-workers.[3,4] A gas mixture of 3% furan plus 3% hydrogen chloride in argon was pulsed into the evacuated microwave cavity consisting of 28-cm diameter spherical mirrors.

The "free induction decay" emission signal following the microwave pulses was digitized, averaged, and Fourier transformed to obtain the spectra. Transtions observed for furan–H^{35}Cl were $3_{03} \rightarrow 4_{04}$, $4_{14} \rightarrow 5_{15}$, $4_{04} \rightarrow 5_{05}$, $4_{23} \rightarrow 5_{24}$, $4_{22} \rightarrow 5_{23}$, $4_{13} \rightarrow 5_{14}$, $5_{15} \rightarrow 6_{16}$, $5_{05} \rightarrow 6_{06}$, $5_{24} \rightarrow 6_{25}$, $5_{23} \rightarrow 6_{24}$, and $5_{14} \rightarrow 6_{15}$. Hyperfine structure due to the ^{35}Cl quadrupole coupling was observed on all transitions and aided in the assignment of rotational quantum numbers to the observed transitions. The observed spectral line positions followed the pattern expected for a planar molecule.

The line centers were fit by using the rotational constants A, B, and C and distortion constants D_{JK} and D_J as adjustable parameters. Values obtained are $A = 9499$ (26) MHz, $B = 1003.93$ (1) MHz, $C = 904.32$ (1) MHz, $D_{JK} = 228.892$ (2) kHz, and $D_J = 0.24$ (17) kHz.

The inertial defect is 2.25 amu Å^2, which is not excessively large for a planar complex of this type. Similar values were obtained for the planar "T"-shaped complexes involving acetylene and hydrogen halides. The experimentally determined geometries of HCl[5] and furan[5,6] were used in order to obtain the structure of the complex. It would be expected that the H–Cl bond length would increase slightly on complex formation, but since the H atom is close to the center of mass of the complex, this would not

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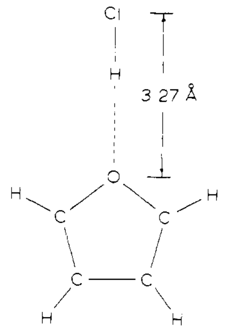

Figure 1. Structure of the furan–HCl complex. The complex is planar.

significantly affect the reported oxygen–chlorine distance.

The rather short oxygen chlorine distance of 3.27 Å and small value observed for D_J indicate strong binding between furan and HCl. If the H–Cl distance were to remain at the free molecule value of 1.3 Å, the O- - -H hydrogen bond length would be 1.97 Å. The corresponding distance is 2.3 Å for benzene–HCl.[7] The structure of the complex is shown in Figure 1. The observed hydrogen bond length of 1.97 Å is significantly longer than the calculated value[1] of 1.783 Å. Molecular orbital calculations do not appear to give as accurate structures for complexes as for the free molecules. The fact that the observed A rotational constant of 9499 MHz for the complex is very close to the A rotational constant of 9447 MHz for free furan strongly suggests the C_{2v} structure shown in Figure 1 with the HCl along the a axis. We have obtained data on the DCl and $H^{37}Cl$ isotopic species, and these data also support the structure given. Work is continuing on this project.

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Registry No. Furan, 110-00-9; HCl, 7647-01-0.

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Intramolecular Exciplexes of Polychromophoric Molecules[1]

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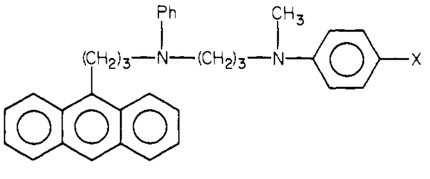
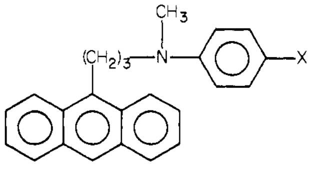
Photoexcited aromatic hydrocarbons form exciplexes with a variety of donors and acceptors.[2] Exciplexes of order higher than 2 are also known which may play important roles in photochemical reactions.[3-12] Light-induced electron transfer in molecular complexes of multiple components has been implicated as the primary step in photosynthesis.[13] However, properties of excited molecular complexes and exciplexes of higher order remained substantially uncharacterized, particularly the role of such complexes in charge transfer.[14] So that the formation and decay of such exciplexes could be probed, polychromophoric molecules of general structures **1** and **2** were synthesized and their spectroscopic properties examined. We concluded that intramolecular ternary exciplexes were formed from **1** under certain experimental conditions, and we were able to determine the factors governing their formation and decay.



1a, X = H
1b, X = OCH_3
1c, X = CH_3



2a, X = H
2b, X = OCH_3

Compounds **1a–c** were synthesized by a conventional method.[15] Compounds **2a,b** were obtained by known routes.[16] Fluorescence spectra of these compounds were measured with a Perkin-Elmer MPF-4 spectrofluorimeter equipped with an electronic corrected spectrum unit and a thermostatic sample compartment, and fluorescence lifetimes were determined via the time-correlated single-photon-counting technique with an apparatus described elsewhere.[17] The fluorescence data are listed in the Table I.

Charge-transfer interaction between components in exciplexes plays an important role in both their stability and decay.[18-20] In solvents of low to medium polarity, this interaction may be analyzed quantitatively by the dependence of fluorescence maximum on the solvent polarity according to the following equation:

$$\bar{\nu}_{ex} = \bar{\nu}_{ex}(0) - (\mu_{ex}^2/hca^3)(f - \tfrac{1}{2}f') \qquad (1)$$

where $\bar{\nu}_{ex}$ is the fluorescence maximum of the exciplex in a given solvent (in cm^{-1}), $\bar{\nu}_{ex}(0)$ is the maximum in vacuo, μ_{ex} is the dipole

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[1] Dedicated to Professor George H. Büchi on the occasion of his 60th birthday.

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