Bimanes. *syn*-(Hydro, ethynyl)bimanet

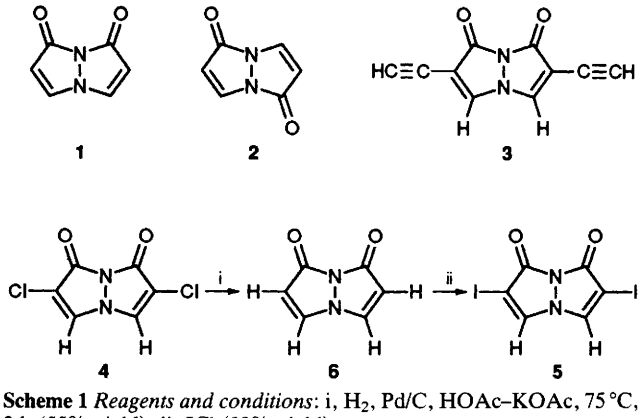
E. M. Kosower,* M. Ben-Shoshan and I. Goldberg

Biophysical Organic Chemistry Unit, School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, Tel-Aviv 69978, Israel

The simplest difunctional monomeric bimane for polymerization *via* the acetylene group, *syn*-(hydro, ethynyl)bimane, has been prepared, and its crystal structure determined.

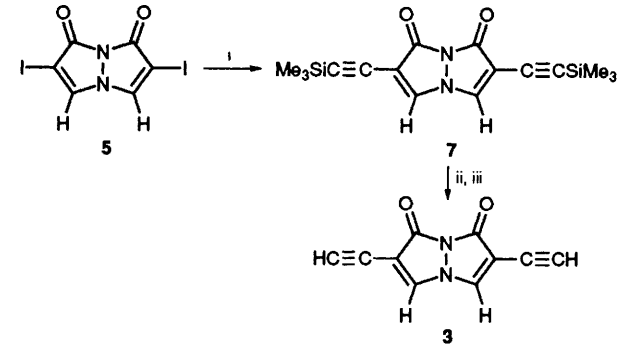
Bimanes (1,5-diazabicyclo[3.3.0]octadienediones)[1-3] are attractive monomers for rod-like polymers. Both *syn* (**1**) and *anti* (**2**) forms would be of value as component units. To create a rod-like polymer, an ethynyl (acetylene) linkage would be useful,[4] having both high bond strength and linear geometry. We now report the synthesis of the simplest model, *syn*-(hydro, ethynyl)bimane **3** and its crystal structure. X-Ray crystallography[5] and thin-film spectroscopy[6] have shown that *syn*-(hydro, chloro)bimane **4** is packed densely in comparison with other organic molecules. Since molecular packing has a critical influence on many polymer properties, the crystal structure of bimane acetylenes with hydrogen at the β-position is of interest.

Compound **5** was prepared from **4**[2] *via* reduction to **6** and iodination (Scheme 1). Among the α-halogeno bimanes, only the α-iodo derivatives are reactive in Pd^0-catalysed coupling with acetylenes. Compound **5** undergoes a Pd-catalysed reaction with trimethylsilylacetylene in acetonitrile to give *syn*-(hydro, trimethylsilylethynyl)bimane **7** in 66.8% yield. Minor amounts of the iodo–trimethylsilylethynyl (3.8% yield), and hydro-trimethylsilylethynyl derivatives (1.2% yield) are also formed. Desilylation of **7** was carried out most effectively with $AgNO_3$ in ethanol followed by LiBr[7] to give **3** in fair yield (Scheme 2). Compound **3** was isolated as a yellow powder from which red–orange crystals were obtained on crystallization. Single crystals of **3** were obtained from acetonitrile solution by slow evaporation.



1 2 3 4 6 5

Scheme 1 *Reagents and conditions*: i, H_2, Pd/C, HOAc–KOAc, 75 °C, 3 h (55% yield); ii, ICl (80% yield)



5 7 3

Scheme 2 *Reagents and conditions*: i, $(Ph_3P)_2PdCl_2$, CuI, $Me_3SiC{\equiv}CH$, Pr^i_2NEt, MeCN, 16 h, 20 °C (67% yield); ii, $AgNO_3$, EtOH, 40 °C, 30 min; iii, LiBr, H_2O, 30 min (66% yield)

† 3,7-Diethynyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione.

The α-trimethylsilylethynyl derivative **7** is stable to air and moisture and can be kept at room temperature without any precautions. The α-ethynyl derivative **3** changes on standing at room temperature, darkening in colour and forming polymers. Both decompose or polymerize on melting (immobile material appears on TLC); **7** has a lower thermal stability than many simple bimanes.[1]

The electronic absorption maximum for the α-trimethylsilylethynyl derivative **7** occurs at longer wavelengths [430 nm (ε 3300)] than that for the corresponding desilylated derivative **3** [410 nm (ε 10 000)] in acetonitrile. Both compounds **7** [λ_{max} 473 (ϕ_F 0.95)] and **3** [λ_{max} 460 (ϕ_F 0.82)] exhibit strong fluorescence in acetonitrile solutions that is shifted to longer wavelengths in the solid, the change for **3** (λ_{max} 535) being greater than that for **7** (λ_{max} 510). The conjugation of the bimane ring with the triple bond in **3** results in a red shift of *ca.* 30 nm with respect to the corresponding dimethyl derivative (λ_{max} 373 nm) in MeCN.

IR spectra are consistent with the structure.[8,9] In the ^1H NMR spectrum of **7** in $CDCl_3$ solution, the β-proton resonates at δ 7.577. Compound **3** is insoluble in $CDCl_3$; in CD_3CN, the β-proton signal is at δ 8.023 and the acetylene proton at δ 3.743. For comparison, the signal for the β-proton in the parent unsubstituted bimane is at δ 7.76 in CD_3CN.[10]

The crystal structure of compound **3** has been determined.‡ The geometric data for bonds and angles are given in Fig. 1. The molecules are located on twofold rotational axes coincid-

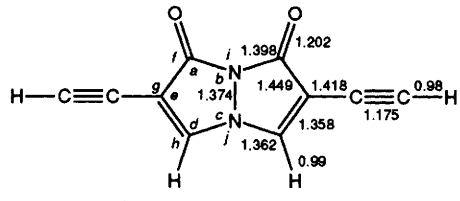


Fig. 1 Bond distances (Å); bond angles (°), **a**, 104.9; **b**, 108.5; **c**, 109.6; **d**, 108.6; **e**; 108.3; **f**, 129.7; **g**, 125.1; **h**, 121; **i**, 142.9; **j**, 140.8

‡ *Crystal data* for **3**: $C_{10}H_4N_2O_2$, M = 184.16, monoclinic, space group $C2/c$, a = 12.518(5), b = 6.621(5), c = 11.016(5) Å, β = 119.33(3)°, V = 796.0 Å^3, Z = 4, D_c = 1.537 g cm^{-3}. The crystal structure was solved by a combination of direct methods and Fourier techniques.[11] The refinement was carried out by full-matrix least-squares methods, including the positional and anisotropic thermal parameters of all the nonhydrogen atoms. Refinement converged at R = 0.045 for 442 observations with $I > 3\sigma(I)$. Best convergence was obtained assuming that the *syn*-bimane framework exhibits partial 180° rotational disorder (82 : 18) about the central long axis through C-3 and C-7. The difference between the sites arises because the chains of hydrogen-bonded molecules do not strictly alternate in direction. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

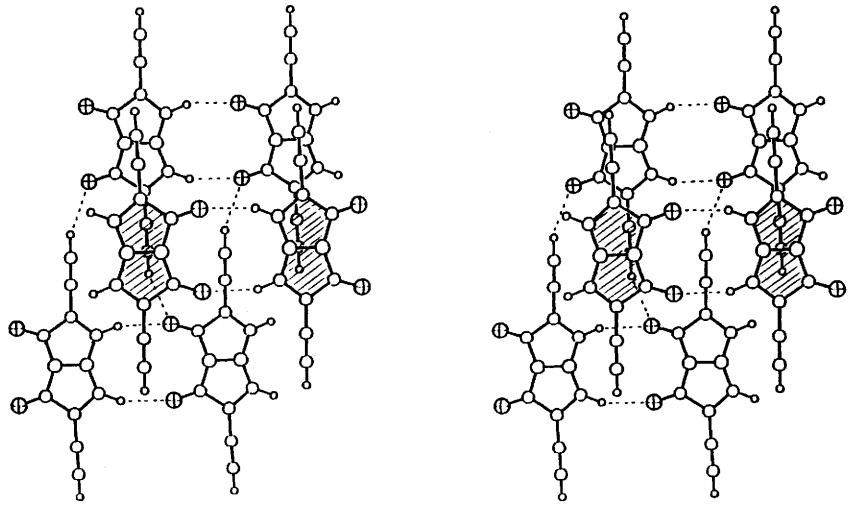


Fig. 2 A perspective view of the structure of **3**, showing the two types of intermolecular hydrogen bonding and how the ethynyl group of a bimane in one layer lies over the bimane ring in the next layer

ing with the N–N bond. Fig. 2 shows the intermolecular crystal packing, indicating the hydrogen bonding interactions and the relationship of the ethynyl group to the bimane in the adjacent layer.

The bond distances and angles shown in Fig. 1 are similar to those observed previously in a number of bimanes.[5,12] The molecular packing is tight and the density of 1.537 g cm^{-3} is quite high for a CHNO compound. The crystal consists of layers of planar molecules with adjacent layers being related by inversion. Within a layer, each molecule associates through hydrogen bonding to six other molecules. Parallel to the *b* axis of the crystal, there is hydrogen bonding between the β-hydrogens with the carbonyls of another molecule, C–H···O 3.22 Å and H···O 2.3 Å. Along the other direction, the hydrogen bonding is between the acetylenic proton to the carbonyl of an adjacent molecule in the layer, C–H···O 3.38 Å. The acetylenic moieties lie parallel to one another with an average distance of 3.3 Å between each layer.

The interlayer stacking arrangement is stabilized by the electrostatic interaction of antiparallel C=O dipoles. The ethynyl group of one molecule is above the nearest five-membered ring of its neighbours, a feature reminiscent of the position of the chlorine in the structure of the dichloro compound **4**.[5] The crystal structure indicates that **3** is interesting as a monomeric unit for polymeric materials in view of the tight packing and the proximity of the acetylenic moieties.

Partial support by the US–Israel Binational Science Foundation through grant 87-00091 and the Basic Research Foundation, Israel Academy of Sciences (grant 157/89), is acknowledged.

Received, 25th May 1993; Com. 3/02991C

References

1 E. M. Kosower and B. Pazhenchevsky, *J. Am. Chem. Soc.*, 1980, **102**, 4983.
2 E. M. Kosower, D. Faust, M. Ben-Shoshan and I. Goldberg, *J. Org. Chem.*, 1982, **47**, 213.
3 E. M. Kosower, D. Zbaida, M. Baud'huin, D. Marciano and I. Goldberg, *J. Am. Chem. Soc.*, 1990, **112**, 7305.
4 J. K. Stille, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 508; J. K. Stille, *Pure Appl. Chem.*, 1985, **57**, 1771; J. K. Stille and J. W. Labadie, *J. Am. Chem. Soc.*, 1983, **105**, 6129.
5 I. Goldberg and E. M. Kosower, *J. Phys. Chem.*, 1982, **86**, 332.
6 E. M. Kosower, J. Hermolin, M. Ben-Shoshan and D. Faust, *J. Org. Chem.*, 1981, **46**, 4578.
7 H. M. Schmidt and J. F. Arens, *Rec. Trav. Chim. Pay-Bas*, 1967, **86**, 1138.
8 L. J. Bellamy, *Infrared Spectra of Complex Molecules*, 3rd edn., Chapman and Hall. London. 1975.
9 J. Tendil and M. Verney, *Tetrahedron Lett.*, 1972, 4023.
10 E. M. Kosower, E. Faust, M. Ben-Shoshan and I. Goldberg, *J. Org. Chem.*, 1982, **47**, 213.
11 P. Main, M. M. Woolfson, L. Lessinger, G. Germain and J. P. Declercq, MULTAN 74, Universities of York and Louvain.
12 J. Goldberg, J. Bernstein, E. M. Kosower, E. Goldstein and B. Pazhenchevsky, *J. Heterocycl. Chem.*, 1983, **20**, 903.