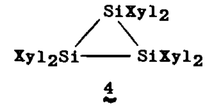
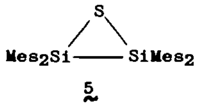
Chart I

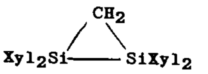


4



5

	4	5
d(Si–Si)	237.5–242.5	228.9
∠'s, Si*	346.5–349.4	357.4



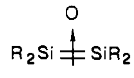
6

	6
d(Si–Si)	227.2
∠'s, Si*	357.4–357.7

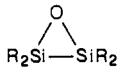
*Sum of ∠'s C–Si–Si', C'–Si–Si', C–Si–C'

in Figure 2. Another surprising feature of the disilaoxirane structure **2a** is the short Si–Si distance, only 222.7 pm, which is more similar to that of a Si–Si double bond (216 pm) than a normal Si–Si single bond (235 pm).

In consideration of the both the short Si–Si bond length and the planar conformation of atoms at silicon, we propose a bonding model in which a significant amount of the double bond character of the disilene is retained in the oxirane. This view is further supported by the silicon-29 NMR coupling constant, ^1J(Si–Si), for an unsymmetrical oxirane, $Xyl_2Si(O)SiR_2$, where R = 2,6-dimethyl-4-*tert*-butylphenyl. The measured value of 99 Hz is again intermediate between that for tetraaryldisilenes (155 Hz)[8] and organodisilanes (85 Hz).[9] All these facts suggest that the disilaoxiranes have some of the character of disilene–oxygen π-complexes A as well as oxiranes B.



A



B

This interpretation of the data is consistent with a theoretical treatment that Cremer[10] has developed to describe the continuum between three-membered rings (3MR) and π-complexes in the ethylene system, C–C–X. This model predicts increased π-complex character, and thus a shortening of the olefinic bond, as the electron acceptor ability of X toward the π-bond increases. The Cremer model may also apply to 3MR containing two silicon atoms, Si–Si–X. In **2a**, the Si–Si π-bond should be a powerful electron donor and the oxygen atom an excellent electron acceptor, leading to a large amount of charge transfer and hence significant π-complex character.[11]

Related compounds with known structures include cyclotrisilane **4**,[1b] disilathiirane **5**[12] and disilacyclopropane **6**.[13] (Chart I). Compounds **5** (X = S) and **6** (X = CH_2) may represent intermediate cases, with shortening of the Si–Si bond and flattening of the configuration about silicon but less extreme than in **2a**.

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Supplementary Material Available: Tables of crystallographic data, atomic coordinates and anisotropic thermal parameters, and bond distances and angles (4 pages); listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Molecular Recognition: Watson–Crick, Hoogsteen, and Bifurcated Hydrogen Bonding in a Model for Adenine Recognition

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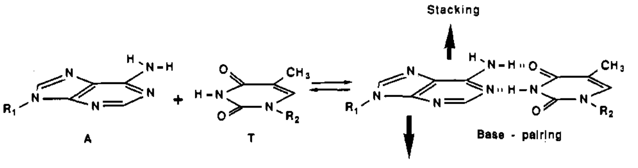
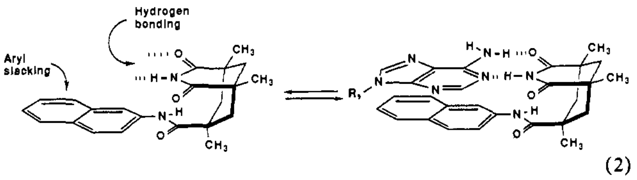
Received June 1, 1987

The principal intermolecular forces that stabilize double-stranded nucleic acids involve Watson–Crick hydrogen bond base-pairing sense and aryl stacking interactions between adjacent base pairs[1] (eq 1). In an effort to dissect the relative contributions of these forces to the overall stability, we recently introduced a model system in which stacking and hydrogen bonding converge from perpendicular directions to recognize and complex adenine derivatives[2] (eq 2). Previously we explored the effects of surface area and molecular chelation on the binding event, and in this communication we are concerned with the geometric details involved in the hydrogen bonds to adenine.



(1)



(2)

Spectroscopic methods involving NOE techniques[3] were used to map out the geometries in the intermolecular complex. Resonance assignments were made for both anthraquinone **1** and 9-ethyladenine (**2**), and, following the determination of relaxation times, pulse sequences were designed for experiments involving intermolecular NOE (heteronuclear and homonuclear) in the complex. In $CDCl_3$ at ambient temperature the association constant is known[2] to be $K_a = 220\ M^{-1}$, and at typical NMR concentrations roughly 50% of the components are bound as a 1:1 complex. The K_a's are determined by Hildebrand–Benesi or Eadie[4] treatment of the binding data in the range of 0.2–15 equiv

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[1] Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984; Chapter 6.

[2] Rebek, J., Jr.; Askew, B.; Buhr, C.; Jones, S.; Nemeth, D.; Williams, K.; Ballester, P. *J. Am. Chem. Soc.* **1987**, *109*, 5033–5035. The K_a for eq 2 is erroneously reported as 120 M^{-1} in the previous paper.

[3] For another recent application of this method, see: Pirkle, W. H.; Pochapsky, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 5627–5628.

[4] Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. Hofstee, B. H. J. *Nature (London)* **1959**, *84*, 1296. Eadie, G. S. *J. Biol. Chem.* **1942**, *146*, 85.

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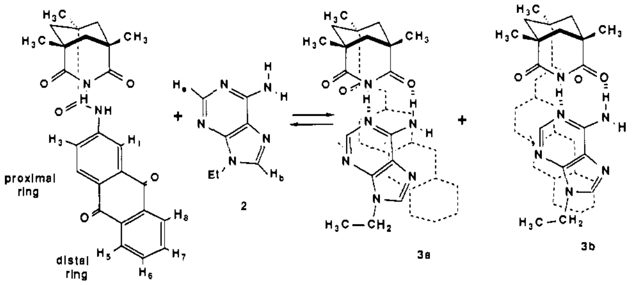
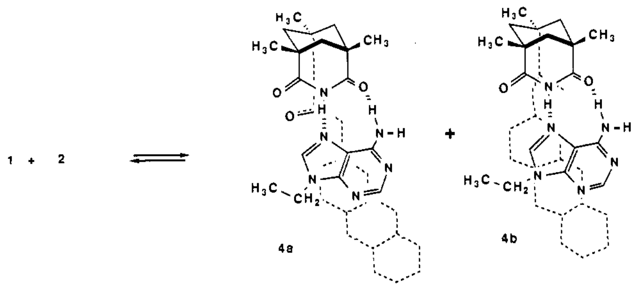
of 9-ethyladenine.[5] Selective irradiation of the methylene group of 9-ethyladenine resulted in enhancements of the proton signals in both the proximal and distal rings of the anthraquinone surface. Two conformations, **3a** and **3b** (eq 3), can be conceived for Watson–Crick base pairing and these are related by rotations around the nitrogen aryl bond. While one seems more favorable to overall aromatic contacts of the van der Waals sort, the NOE's observed in this experiment 3.3% and 3.9%, for $H_{5,8}$ and $H_{6,7}$, respectively, indicate that both conformations contribute to the structure of the Watson–Crick type complex.[6]



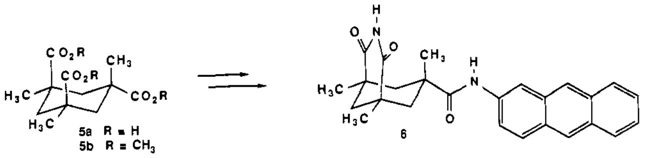
(3)

In the same experiment, NOE's were also observed for protons in the proximal ring, specifically H_1 and H_3, showing a 3% enhancement on irradiation of the methylene of **2**. This result cannot be rationalized on the basis of exclusive Watson–Crick base pairing but is nicely accommodated by the Hoogsteen[7] base pairings **4a** and **4b** shown in eq 4.



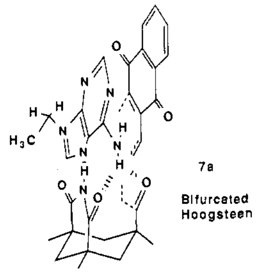
(4)

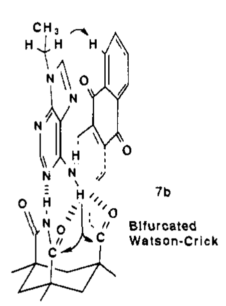
Parallel experiments with the cis/trans isomer[8] (eq 5) provide a series of control experiments. In structure **6**, both intermolecular forces are available but cannot act simultaneously. Indeed, no such intermolecular NOE's were observed between the methylene of **2** and the aromatic surface of **6** in its complex (K_a = 60 M^{-1}).



(5)

In heteronuclear experiments, irradiation of the NH bond of the adenine derivative **2** led to enhancements of the ^{13}C signals of both imide carbonyls (20%) as well as the amide carbonyl (24%) indicated in **7a** and **7b**. The simplest explanation would invoke bifurcated hydrogen bonds in which the amino NH is in simultaneous contact with both carbonyls as suggested in the structures.


7a
Bifurcated Hoogsteen


7b
Bifurcated Watson-Crick

Again, parallel experiments involving **6** in the complexes of **1** showed only enhancements of the imide carbonyl (11%). A bifurcated hydrogen bond appears preferred in the complex as of **1** even though a near perfect match in the Watson–Crick sense is presented by the imide portion.[9] The bifurcation in this system could be reinforced by the natural tendency of A–T base pairs to undergo a propellerlike twist in double-stranded DNA.[1]

In summary, the model system permits direct observation of Watson–Crick, Hoogsteen, and bifurcated hydrogen bonds, and the relative contributions of each can now be assessed.[10] It is our intent to use these new systems as a probe with intact nucleic acids in more biologically relevant media.[11]

Acknowledgment. We thank the National Science Foundation for support of this research.

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(5) For earlier studies involving hydrogen bonding and stacking in models, see: Kyogoku, Y.; Lord, R. G.; Rich, A. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *57*, 250–257. Hammes, G. C.; Park, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 4151–4157. Chan, S. I.; Schweitzer, M. P.; Tso, P. O. P.; Helmkamp, G. K. *J. Am. Chem. Soc.* **1964**, *86*, 4182. Schweitzer, M. P.; Chan, S. I.; Tso, P. O. P. *J. Am. Chem. Soc.* **1965**, *87*, 5241. Iwahashi, H.; Kyogoku, Y. *J. Am. Chem. Soc.* **1977**, *99*, 7761–7765.

(6) Intramolecular enhancements observed between the imide N-H and H_1 and H_3 in the complexation experiments also support two conformations of the anthraquinone nucleus. Intermolecular NOE's between the imide N-H and both H_a and H_b of the adenine derivative are also observed.

(7) Hoogsteen, K. *Acta. Crystallogr.* **1963**, *16*, 907–916.

(8) Prepared as described for the cis,cis isomer in ref 2. All new compounds showed the expected high resolution spectroscopic features for **5a**, mp 205–215 °C, and **6**, mp 330–336 °C. Structure **5b** is a byproduct in the production of the cis,cis triacid: Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426–2431.

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Infrared Spectroscopy of Matrix-Isolated Propadienone

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Traditional valence bond theory predicts that propadienone ($H_2C{=}C{=}C{=}O$) should possess a linear heavy atom chain and that it should resemble formaldehyde more closely than ketene in its physical and chemical properties.[1] Since propadienone was first detected in 1976,[2,3] lively debate has ensued about its geometric and electronic structure.[4-8] Results from microwave spectroscopy contradict the valence bond predictions and show that the heavy atom chain is bent.[6-8] Calculations agree with this

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[†] Present address: Merck Sharp & Dohme Research Laboratories, West Point, PA 19486.

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