

Rapid, base-catalyzed epimerization at C-1'¹⁶ precluded application of the standard formylation-diazo transfer protocol^{17,18} to the preparation of diazoketone **8**. However, activation of the 3'-carbon was readily achieved by heating the ketone **6** in neat *N,N*-dimethylformamide dimethyl acetal at 60 °C for 15 min to give the enamino ketone **7** in 80% yield. The observation of NOE's¹⁹ between H-1' and H-4' and H-5' and H-8 verified that the stereochemistry at C-1' had been preserved in this unusually facile reaction.²⁰ In contrast, diazo transfer^{21a} to the enamine^{21b} proved to be unusually difficult. After the enamine failed to react with excess tosyl azide in refluxing toluene, we were delighted to find that diazo transfer from triflyl azide²² in 1,2-dichloroethane at 60 °C was complete in just 2 h. Application of the reaction mixture to a column of silica gel packed in ethyl acetate/hexane and elution with the same solvents (1:3 to 10:0) yielded the diazoketone **8** as a light yellow solid. Salient spectral features of this compound included a strong IR absorption at 2115 cm⁻¹ (C=N⁺=N⁻), a doublet of doublets ($J = 7.5$ Hz, $J' = 5.0$ Hz) at 5.44 ppm assigned to the 4' hydrogen, and an (M + H)⁺ = 494.1971 (calcd mass for C₂₃H₂₈N₇O₂Si = 494.1972). In the key step, irradiation of the diazoketone **8** in methanol with a 450-W, Pyrex-filtered, Hanovia lamp for 30 min at room temperature produced the oxetanes **9α** and **9β**, the products of Wolff rearrangement.²³⁻²⁵ Separation of the diastereomeric oxetanes from each other and from the ketone **6** (12%)²⁶ and *N*⁶-benzoyladenine (25%)²⁷ was achieved by chromatography on silica gel. NOE's between the 2' and 5' and 2' and 8 protons established that the major diastereomer (**9α**, 24%, $[\alpha]^{25}_D -18.4^\circ$ (*c* 1.58, CHCl₃)) possessed the all-trans stereochemistry of oxetanocin. The absence of these NOE's in the minor, all-cis diastereomer (**9β**, 12%, $[\alpha]^{25}_D +27.6^\circ$ (*c* 1.01, CHCl₃)) and the presence of an NOE between the 8 and 5' protons confirmed that the Wolff rearrangement had proceeded with complete retention of configuration.²⁸ Treatment

of the major epimer with excess NaBH₄ in ethanol rapidly reduced the methyl ester and then, more slowly, effected N-debenzoylation to give the monoprotected alcohol **10** (74%), a valuable intermediate for further modification.²⁹ Addition of 1.7 equiv of trimethylsilyl chloride to a solution of **10** in methanol followed by neutralization with Dowex-SBR (OH⁻) resin released oxetanocin (**1**) in nearly quantitative yield. The identity of the synthetic ($[\alpha]^{25}_D -41.3^\circ$ (*c* 0.65, pyridine)) and natural ($[\alpha]^{20}_D -44.3^\circ$ (*c* 0.21, pyridine))⁴ material was established by direct comparison (TLC, MS, 300 MHz NMR) with an authentic sample. In particular, the chemical shifts of their ten ¹³C NMR (125.8 MHz) resonances in D₂O differed by less than ±0.03 ppm. In summary, (-)-oxetanocin has been synthesized in 12 steps from adenosine in an overall yield of 5%. Application of this methodology to the preparation of pyrimidine analogues of oxetanocin is in progress.

Acknowledgment. We are grateful to Randal Chen for providing a sample of natural oxetanocin and Patricia Pavlik and David Whittern for assistance in obtaining spectral data.

Supplementary Material Available: Spectral and physical data for compounds **1** and **5-10** (3 pages). Ordering information is given on any current masthead page.

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The Structure of 1,4-Cyclohexadiene at 153 K

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The minimum energy conformation of 1,4-cyclohexadiene (1,4-dihydrobenzene)¹⁻⁸ has become a subject of renewed interest because of recent research on the structure of its cis and trans substituted and condensed ring derivatives.⁹⁻¹⁴

There are conflicting conclusions concerning the structure of the parent molecule in the gas phase. One electron diffraction study concluded that the molecule was planar or nearly planar,³ but a later study⁶ favored a nonplanar molecule with C_{2h} symmetry and a dihedral angle of 159° between the ethylene planes. The boat conformation was apparently favored,⁹ although the vibration, rotational Raman, and NMR spectra were best interpreted as

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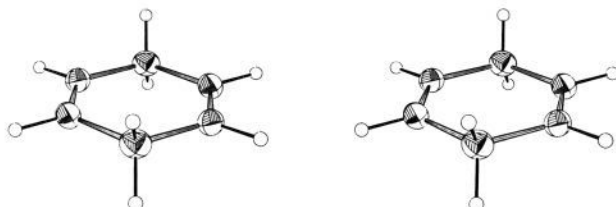
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Table I. Atomic Parameters for 1,4-Cyclohexadiene at 153 K^a

atom	x	y	z	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.1182 (2)	0.4113 (2)	0.9059 (1)	3.57 (8)	4.04 (8)	4.07 (8)	-0.05 (7)	0.21 (6)	-0.83 (6)
C(2)	0.0082 (2)	0.5470 (2)	0.8626 (1)	4.17 (8)	4.55 (8)	3.39 (8)	-0.43 (7)	-0.21 (7)	0.13 (6)
C(3)	0.1227 (2)	0.3472 (2)	1.0485 (2)	4.02 (9)	4.43 (9)	4.86 (9)	0.77 (8)	-0.46 (7)	0.21 (7)
H(1)	0.199 (2)	0.346 (2)	0.845 (1)	4.6 (4)					
H(2)	0.006 (2)	0.581 (2)	0.765 (2)	5.4 (4)					
H(3)	0.094 (2)	0.211 (2)	1.054 (1)	6.8 (5)					
H(4)	0.253 (2)	0.352 (2)	1.079 (1)	5.4 (4)					

^a U_{ij} and U in $\text{\AA}^2 \times 100$. The temperature factors are of the following form: $T(\text{aniso}) = \exp(-2\pi^2\{U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*\})$; $T(\text{iso}) = \exp(-8\pi^2U \sin^2 \theta/\lambda^2)$.

**Figure 1.** Stereoview²² of the X-ray structure of 1,4-cyclohexadiene at 153 K. Thermal ellipsoids are drawn at 50% probability.

evidence for the planar structure. An early molecular mechanics calculation⁸ favored an averaged structure across a shallow boat–boat inversion potential. Two later ab initio molecular orbital calculations predicted a planar structure with a shallow potential in the direction of the boat distortions.^{15,16}

We have determined the crystal structure of C_6H_8 , mp 223 K, at 153 K. Crystallization was at 200 K directly on the X-ray diffractometer using a procedure described elsewhere.¹⁷ While cooling down no phase transition was observed, though expected to be at 193 K as a previously taken DTA suggested. Further attempts to obtain the low-temperature phase were not successful. The crystal structure is orthorhombic, *Pbca* with four molecules in the unit cell (as for benzene¹⁸). In the absence of disorder, the molecular symmetry is required to be $\bar{1}$, which is a planar or chair ring conformation. The diffraction data were collected at 153 K on a crystal of the supercooled high-temperature form. The intensities of 444 unique reflections, of which 31 had $|F_o| < 2\sigma$, were measured with Zr-filtered Mo $K\alpha$ radiation. The unit cell dimensions at 153 K are $a = 7.070$ (3), $b = 7.169$ (2), and $c = 9.909$ (2) \AA . The structure was solved by using SHELXS-86,¹⁹ and the parameters were refined by using XTAL²⁰ to disagreement factors of $R = 0.037$, $R_w = 0.034$ ($w = \sigma(F_o)^{-1}$) for 44 parameters. The final difference maps showed no peaks greater than 0.15 $e\text{\AA}^{-3}$. The atomic parameters are given in Table I.

The carbon atom ring is planar within 0.002 \AA (see Figure 1). The root-mean-square displacements of the carbon atoms perpendicular to the plane of the molecule, calculated from the anisotropic thermal motion tensors, are C(3) 0.22 (3), C(1) 0.19 (3), and C(2) 0.20 (3) \AA . Although that of C(3) is longer than for C(1) and C(2), the differences are not significant. There is therefore no evidence of any disorder involving a boat, or chair, conformation. However, it is important to remark that disorder involving very small distortions from planarity can never be excluded by means of a crystal structure analysis at one temperature.

The C–C bond lengths and angles are compared with those reported from the other studies in Table II. The C–H bond

Table II. Bond Lengths and Valence Angles in 1,4-Cyclohexadiene

	this work ^a	electron diffrctn ^b	electron diffrctn ^c	ab initio MO ^d	ab initio MO ^e
C(1)=C(2)	1.318 (2)	1.347 (4)	1.334 (2)	1.309 (1.339)	1.317
C(1)–C(3')	1.486 (2)	1.511 (4)	1.496 (1)	1.522 (1.511)	1.509
C(2)–C(3)	1.486 (2)				
C(1)–C(3')–C(2')	113.1 (1)	(111.9)	113.3 (3)	112.3	112.4
C(1)–C(2)–C(3')	123.5 (1)	122.7 (3)	123.4 (6)	120.4	123.8
C(3')–C(1)–C(2)	123.4 (1)				

^aUncorrected for thermal motion, estimated corrections +0.005 \AA .¹⁸ Distances in \AA , angles in deg. ^bReference 6. ^cReference 3. ^dUsing GAUSSIAN with STO-3G.¹⁵ The values in parentheses are corrected from STO-3G to MP2/6-31G* by the offset method using C–C in C_2H_6 and C=C in C_2H_4 .²¹ ^eUsing MOLECUL with (7,3) \rightarrow (4,2) for C, (4) \rightarrow (2) for H.¹⁶

lengths are 0.95 to 1.00 \AA , with H–C(3)–H = 103 (1)°.

Acknowledgment. Research was supported by the Fonds der Chemischen Industrie (FRG) and the U.S. National Science Foundation through Grant CHE-8610668 (G.A.J.). We are grateful to Professor A. K. Cheetham of Oxford University, UK, for bringing this problem to our attention.

Supplementary Material Available: List of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Achieving High Quantum Yield Charge Separation in Porphyrin-Containing Donor–Acceptor Molecules at 10 K

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Received April 18, 1988

A long-standing problem in the study of porphyrin- and chlorophyll-based donor–acceptor compounds designed to mimic photosynthesis is the failure of most of these molecules to undergo high quantum efficiency photoinitiated charge separation in the solid state at very low temperatures.¹ The rate constants for oxidation of the lowest excited singlet states of porphyrin donors by acceptors decrease sharply at the freezing points of the media in which the compounds are dissolved.¹ This results in a small or negligible quantum yield of charge separation because the rate of electron transfer cannot compete with the decay of the porphyrin excited singlet state to ground state. This behavior contrasts sharply with the slight increase in rate for primary electron transfer exhibited by photosynthetic reaction centers upon cooling to 4.2

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