attempt to determine the applicability of this rule to open-chain compounds and other sized rings.

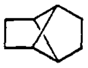
Acknowledgment. Part of this work was done with the support of National Institutes of Health Grant HD-01281, for which financial assistance is acknowledged.

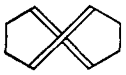
Marvin Carmack, Leonard A. Neubert
Department of Chemistry, Indiana University
Bloomington, Indiana 47401
Received July 17, 1967

trans,trans-1,5-Cyclooctadiene[1]

Sir:

Irradiation of *cis,cis*-1,5-cyclooctadiene in an ether solution containing copper(I) chloride yields tricyclo-$[3.3.0.0^{2,6}]$octane (**1**).[2] The mechanism of this reaction is still unclear;[2] however, the fact that the carbon skeleton of **1** can in principle be derived in a simple manner from the racemic conformation of *trans,trans*-1,5-cyclooctadiene (**3a**) makes the properties of this latter hydrocarbon under the conditions of the photochemical reaction of interest. We wish to report the isolation of both *cis,trans*-[3] and *trans,trans*-1,5-cyclooctadienes from an irradiated pentane suspension of bis[chloro(*cis,cis*-1,5-cyclooctadiene)copper(I)] (**2**).[4]


1


3a


3b

The crystalline complex **2**, when suspended in pentane, dissociates partially to free cyclooctadiene and a solid nonstoichiometric cyclooctadiene–copper(I) chloride complex containing excess copper(I) chloride. A stirred suspension of **2** (0.5 g, 1.2 mmoles) in 70 ml of degassed pentane was irradiated for 24 hr in a quartz vessel, using a Rayonet reactor equipped with low-pressure mercury lamps. The resulting mixture was filtered, and the solid was washed thoroughly with pentane. The filtrate was shown by vpc to contain **1** (19%, based on the cyclooctadiene originally present in the complex **2**), *cis,cis*-1,5-cyclooctadiene (52%), and small quantities of several other components.[5] The remainder of the olefinic material was bound in the pentane-insoluble copper(I) chloride residue.

The solid residues from several irradiations were combined and treated with aqueous sodium cyanide solution to displace the remaining olefins from their copper(I) complexes. The pentane extract of the resulting mixture contained *cis,cis*-1,5-cyclooctadiene (10% based on **2**), *cis,trans*-1,5-cyclooctadiene (13%; vpc retention time and infrared spectrum identical with those of an authentic sample[3]), and a new compound, **3** (1.5%).[6]

Compound **3** polymerized rapidly in the presence of oxygen or acid, or in concentrated solution, but could be isolated by preparative vpc[6] and stored in dilute pentane solution at −20° for several hours. Its infrared spectrum (CCl_4 or CS_2) showed bands at 1615 (olefin) and 985 cm^{-1} (*trans* olefin), but no bands in the region 750–650 cm^{-1} (*cis* olefin).[7] Its mass spectrum showed a clearly defined molecular ion at *m/e* 108 ($C_8H_{12}^+$) and a fragmentation pattern very similar to that of *cis,cis*- and *cis,trans*-1,5-cyclooctadienes,[8] but easily distinguishable from that of *cis,cis*-1,3- and *cis,cis*-1,4-cyclooctadienes.[9] The nmr spectrum of **3** (1:1 TMS–CCl_4, −20°) showed structureless peaks at δ 4.88 (olefinic hydrogen) and 2.43 (allylic hydrogen), with relative areas 1:2. Ozonolysis of **3** and oxidation of the ozonide gave succinic acid in approximately 85% yield, as determined by vpc analysis of its dimethyl ester following esterification with diazomethane. No (<0.5%) glutaric or adipic acid could be detected in the ozonolysis mixture.

Compound **3** could also be prepared, albeit in low yield (2.4%), by the low-temperature Hofmann degradation[10] of a mixture of *cis*- and *trans*-1,5-bis(dimethylamino)cyclooctane dimethiodides[11] with potassium amide in liquid ammonia. The only other hydrocarbon product detectable by vpc in this reaction was *cis,trans*-1,5-cyclooctadiene (1.2%).

These results show unambiguously that **3** is *trans,trans*-1,5-cyclooctadiene. That the *cis,trans*- and *trans,trans*-1,5-cyclooctadienes are found only in the solid residues from the irradiation, rather than free in solution, is consistent with the known high stability of complexes of cyclic *trans* olefins with silver(I).[12]

The ultraviolet spectrum of *trans,trans*-1,5-cyclooctadienes in both isooctane and ether solutions showed an unusual absorption at λ_{max} 246 mμ (ϵ ~1500). This transition must in some manner owe its low energy to the proximity of the π orbitals of the double bonds of **3**.[13] However, neither this observation, nor the other available spectroscopic data, can presently be interpreted to provide a clear answer to the chemically important question of the relative stabilities of the conformations **3a** and **3b**.

---

[1] Supported in part by the U. S. Army Research Office (Durham), Grant ARO(D)-31-124-435, and by the National Science Foundation, Grant GP-6222.

[2] R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); I. Haller and R. Srinivasan, *ibid.*, **88**, 5084 (1966).

[3] A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *ibid.*, **89**, 4024 (1967).

[4] J. H. van der Hende and W. C. Baird, Jr., *ibid.*, **85**, 1009 (1963); H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).

[5] See J. Meinwald and B. E. Kaplan, *J. Am. Chem. Soc.*, **89**, 2611 (1967), and ref 2 for discussions of the structures of these products.

[6] Vpc analyses were carried out using glass columns containing 4-nitro-4-methylpimelonitrile or 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P; injection and detector block temperatures of 80° were necessary to avoid thermal decomposition of **3**.

[7] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, pp 34–57.

[8] The principal differences were small differences in peak intensities. Mass spectra of *cis* and *trans* olefins are usually almost identical (K. Bieman, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 151).

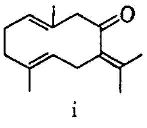
[9] The most intense peak in the mass spectra of **3** and the 1,5-cyclooctadienes occurred at *m/e* 54, attributable to butadiene molecular ion. There were no intense peaks in this region in the spectra of the other isomers.

[10] G. Wittig and R. Polster, *Ann. Chem.*, **612**, 102 (1958).

[11] Z. Jacura, Ph.D. Thesis, Massachusetts Institute of Technology, 1962. The amine was prepared in a straightforward manner from 1,5-cyclooctanedicarboxylic acid [A. C. Cope, E. S. Graham, and D. J. Marshall, *J. Am. Chem. Soc.*, **76**, 6159 (1954)].

[12] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[13] The anomalous absorption displayed by germacrone (i) and its derivatives at 213 mμ (ϵ 12,600) provides some precedent for the spectrum of **3**: F. Sorm, *Pure Appl. Chem.*, **2**, 533 (1961). Although this transition was rationalized by an interaction between parallel double bonds, the endocyclic double bonds in the related germacatriene have been shown to possess the "crossed" conformation by X-ray crystallography of its silver nitrate complex: F. H. Allen and D. Rogers, *Chem. Commun.*, 588 (1967).



i

Irradiation of **3** in pentane gave tricyclooctane **1** in 70% yield, and no other volatile products. We have not been able to convert **3** to **1** thermally under a variety of conditions. The former observation, taken with others which will be published in the complete paper, suggests that *trans,trans*-1,5-cyclooctadiene may be an intermediate in the copper-catalyzed photochemical conversion of *cis,cis*-1,5-cylooctadiene to tricyclooctane (**1**).

Acknowledgment. We gratefully acknowledge the assistance of Dr. A. S. Mehta in the performance of preliminary experiments.

---

[14] National Science Foundation Predoctoral Fellow, 1964–1966; National Institutes of Health Predoctoral Fellow, 1966–1967.

[15] Deceased June 4, 1966.

George M. Whitesides, Gerald L. Goe,[14] Arthur C. Cope[15]
Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts

Received October 20, 1967

Spectroscopic Models Related to Coenzymes and Base Pairs.[1] I. The Basis for Hypochromism in the Ultraviolet Spectra of Model Systems Related to Nicotinamide–Adenine Dinucleotide

Sir:

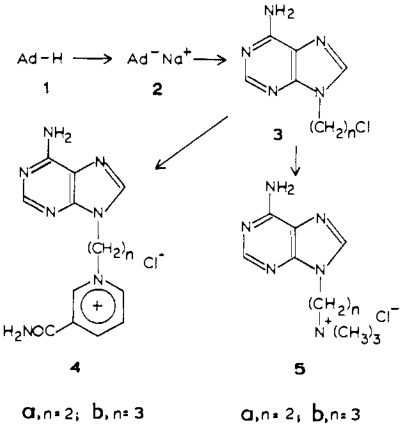
Spectroscopic models have been designed which incorporate aromatic and electrostatic features present in NAD$^+$,[2] *e.g.*, compounds **4** and **5**.[3] Ultraviolet spectroscopic data for **4** should reflect *both* oscillator interaction between the adenyl and the pyridinium rings *and* the possible electrostatic field effect of quaternary nitrogen, whereas the data for **5** should reflect *only* the perturbation of the adenyl chromophore by the positive charge.

Evidence for interaction between the adenyl and pyridinium moieties of NAD$^+$ was obtained by Siegel, *et al.*,[4] who observed decreased adsorbance (8.7%) at the 259-mμ absorption maximum of the intact coenzyme relative to the sum of the absorbancies of the component nucleotides obtained by enzymic hydrolysis. Similar hypochromicity[5] studies were conducted on some NAD$^+$ analogs containing modified adenyl moieties,[6] with the conclusion that the optical anomalies could only be explained by interaction between the component heterocyclic systems.

Although many analogs of the adenine and nicotinamide rings have been incorporated into NAD$^+$ models, and, thus, much attention has been focused on the aromatic moieties involved in the intramolecular interaction, *little attention has been given to models which reflect the possible electrostatic contribution.*

The electrostatic field can be an important factor in a system in which a charge is intimately associated with the chromophore.[8] Moreover, on theoretical grounds it has been demonstrated that hypochromism is a consequence of the effect of the local internal field.[9]

In order to prepare the model compounds Ad-C$_n$-Nic$^+$ (**4**) and Ad-C$_n$-N$^+$ (**5**)[10] designed for ultraviolet study, sodium adenide (**2**)[11] was prepared in DMF from adenine (**1**) and sodium hydride and was alkylated *in situ* with the relevant 1-bromo-*n*-chloroalkane to give the intermediate **3**: **a**, 9-(2-chloroethyl)adenine, mp 206–208°; **b**, 9-(3-chloropropyl)adenine, mp 189–190°. Treatment of **3** with excess nicotinamide in a melt and with excess trimethylamine in tetramethylene sulfone[12] afforded the respective products: **4a**, Ad-C$_2$-Nic$^+$, mp 292–293°; **4b**, Ad-C$_3$-Nic$^+$, mp 255–256°; **5a**, Ad-C$_2$-N$^+$, mp 274–276°; **5b**, Ad-C$_3$-N$^+$, mp 266–268°.



The percentage hypochromism, % $H(\nu)$, for a pair of interacting bases A and B is defined as $[1 - f_{AB}/(f_A + f_B)]100$, where f_{AB} is the oscillator strength of the intact molecule and f_A and f_B are oscillator strengths of the components of the molecule. For example, in calculating the hypochromism of Ad-C$_3$-Nic$^+$, $f_A + f_B$ is the sum of the oscillator strengths of Ad-C$_3$ and Nic$^+$-C$_3$.[3] The ultraviolet absorption curves for NAD$^+$ and the coenzyme models[13] were digitized from the absorption minimum of the 260-mμ (38,460 cm^{-1}) band to the upper wavelength extremity of the band and were compared in absorption intensities with those of the appropriate half-models using the same integration cut-offs.[14]

---

[1] This work was supported in part by a research grant (USPHS-GM-05829) from the National Institutes of Health, U. S. Public Health Service, to whom we are pleased to acknowledge our thanks.

[2] This paper is taken in part from the Ph.D. Thesis of P. C. Huang, University of Illinois, 1966.

[3] The following abbreviations are used: Ad-C$_n$-Nic$^+$ for 1-[*n*-(aden-9-yl)alkyl]-3-carbamoylpyridinium chloride; Ad-C$_n$-N$^+$ for *n*-(aden-9-yl)alkyltrimethylammonium chloride; Ad-C$_3$ for 9-propyladenine, mp 178–179°; Nic$^+$-C$_3$ for 1-propyl-3-carbamoylpyridinium chloride, mp 199–200°.

[4] J. M. Siegel, G. A. Montgomery, and R. M. Bock, *Arch. Biochem. Biophys.*, **82**, 288 (1959).

[5] The term hypochromicity is used to refer to a decrease in the absorbancy at the absorption maximum of an intact molecule relative to the sum of the absorbancies of the constituent chromophores at selected absorption maxima. Hypochromism, on the other hand, corresponds to an integrated hypochromic effect and is based upon the respective total absorption intensities rather than the absorbancies at the absorption maxima.[7]

[6] (a) G. Pfleiderer, C. Woenckhaus, K. Scholz, and H. Feller, *Ann. Chem.*, **675**, 205 (1964); (b) C. Woenckhaus, *Chem. Ber.*, **97**, 2439 (1964).

[7] M. M. Warshaw and I. Tinoco, Jr., *J. Mol. Biol.*, **20**, 29 (1966).

[8] (a) E. M. Kosower and D. C. Remy, *Tetrahedron*, **5**, 281 (1959); (b) V. Georgian, *Chem. Ind.* (London), 930 (1954); 1480 (1957); C. A. Grob, A. Kaiser, and E. Renk, *ibid.*, 598 (1957).

[9] R. K. Bullough, *J. Chem. Phys.*, **43**, 1927 (1965).

[10] Satisfactory analyses and spectral characterizations were obtained for all new compounds reported.

[11] N. J. Leonard, K. L. Carraway, and J. P. Helgeson, *J. Heterocyclic Chem.*, **2**, 291 (1965).

[12] C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **28**, 83 (1963).

[13] The absorption maxima were very similar for the various models [compound (in H$_2$O), $\lambda_{max}^{pH\ 7.0}$ (mμ), $\lambda_{max}^{pH\ 1.0}$ (mμ)]: NAD$^+$, 258.5, 258; Ad-C$_2$-Nic$^+$, 261, 258.5; Ad-C$_3$-Nic$^+$, 261.5, 259.5; Ad-C$_2$-N$^+$, 260, 257; Ad-C$_3$-N$^+$, 260.5, 258; Ad-C$_3$, 261, 259.5; Nic$^+$-C$_3$, 264, 264; NMN, 265.5, 265.

[14] Digitizing was accomplished using a Benson-Lehner Corp. decimal converter Model F instrument. Numerical integration using Simpson's rule was then carried out using an IBM 7094 computer. We