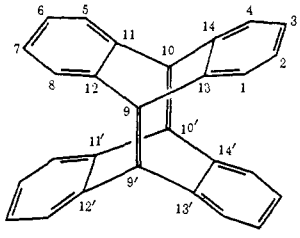
Application of the reaction sequence of Chart I to 9,10′-dibromodianthracene[4] (the photodimer of 9-bromoanthracene) afforded a bistriazoline[6] which was isolated (mp 155° dec) and converted to the bis-*N*-amino derivative (mp 185° dec).[6] Oxidation of the bis-*N*-aminotriazoline with lead tetraacetate in methylene chloride afforded a solid which was chromatographed on silica, recrystallized from benzene, and sublimed: yield of purified material, 20% in the oxidation step; colorless crystals; mp 388° dec (sealed, evacuated capillary); uv (CH_2Cl_2) λ 270 nm (ε 2850), a shoulder tailing toward the visible (ε 1430 at 280 nm, 330 at 300 nm, 12 at 320 nm);[9] in the mass spectrum, the molecular ion is the base peak, *m/e* (relative intensity), 353 (31), 352 (100), 351 (22), 350 (40), 348 (18), 175 (13), 174 (12). (*Anal.* Calcd for $C_{28}H_{16}$: C, 95.42; H, 4.58. Found: C, 95.31; H, 4.51). The compound is stable to heat, air, and moisture.

A complete X-ray analysis has been carried out on this compound, establishing structure I.[10] The crystal has one molecule per unit cell in space group $P\bar{1}$ (*i.e.*, the molecule has a center of symmetry). The cell dimensions (triclinic) are $a = 8.133 \pm 0.0004$ Å, $b = 11.703 \pm 0.001$ Å, $c = 6.551 \pm 0.0008$ Å, $\alpha = 97.16 \pm 0.01°$, $\beta = 107.78 \pm 0.01°$, and $\gamma = 126.01 \pm 0.01°$.

The principal results of the X-ray analysis (final *R* value = 0.052) are summarized in Chart II.

Chart II



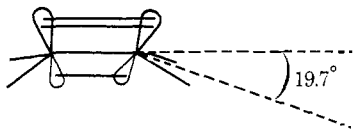
I

Bond lengths,[a] Å	
1–3	1.397
2–3	1.38
1–13	1.38
13–14	1.42
9–13	1.508
9–9′	1.35
Bond angles	
$C_{11-12-9}$	109.7°
$C_{12-9-13}$	109.2°

[a] Average values for the different types of bonds in I.

Four points are of special interest regarding the structure: (1) the bridgehead carbon–carbon double bond distance (observation, $C_{9-9'} = 1.35$ Å); (2) the location of these bridgehead atoms relative to the atoms attached thereto (observation; $C_{9,9'}$ lie 0.50 Å outside the plane defined by the four attached atoms, $C_{12,12',13,13'}$); (3) the distance between the double bonds (observation, $C_{9-10} = 2.42$ Å); (4) the angle between the planes defined by atoms 9, 10, 11, and 12 and atoms 9, 9′, 10, 10′ (observation, 119.9°).

Angle strain at $C_{11-12-9}$ (and equivalent locations) and/or electron repulsion between the two bridgehead double bonds force these double bonds away from each other resulting in a state of hybridization at $C_{9,9',10,10'}$ intermediate between sp^2 and sp^3 and with formation of π bonds distorted as in V, similar to (but not as extreme as) the situation in benzyne.[11]



V

Attempts at direct or sensitized photolysis of I have provided no evidence for the bispropellane II or for 9,10-didehydroanthracene, a possible cleavage product.

An interesting aspect of compound I (and one in great contrast to molecules such as dewarbenzenes) is that, in spite of considerable strain in the molecule, there is no logical stable isomeric or polymeric form to which it might convert. Not unexpectedly, it *is* reactive toward many reagents, an aspect that will be taken up in the full report of this work.

(9) The uv is rather similar to that of dianthracene. For the uv of 9,10-didehydrodianthracene see D. E. Applequist and R. Searle, *J. Amer. Chem. Soc.*, **86**, 1389 (1964).

(10) X-Ray analysis of monoolefin IV (Dr. Alan Parkes, unpublished results) is not definitive on bridgehead positions: (a) unit cell and packing pattern are essentially those of dianthracene; (b) compound IV is "disordered" (randomization of 9,9′ and 10,10′ positions).

(11) For other examples of transient and isolated strained double bonds, see C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *J. Amer. Chem. Soc.*, **95**, 6121 (1973), and references cited therein.

(12) National Science Foundation Predoctoral Fellow, 1968–1971.

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Rotational Barrier in an Allyl Radical

Sir:

Numerous allyl radicals have been investigated by esr spectroscopy,[1,2] but in no case has rotation of an allyl bond been observed. Allylic chlorination of cis–trans isomeric butenes with *tert*-butyl hypochlorite shows that the butenyl radicals are configurationally stable in this reaction up to 40°.[3] Isomerization of these radicals has been found at elevated temperatures ($T = 125°$).[4] The free energy of activation for isomerization of the butenyl radical has been estimated to be $\Delta G^{\ddagger} = 21 \pm 3$ kcal/mol.[4] As the greater part of the rotational barrier should be due to the loss of allyl stabilization, the value is much higher than anticipated from the knowledge of this stabilization (12–14 kcal/mol).[5,6]

For some time we have been studying substituted allyl radicals by esr spectroscopy.[7] A first case in which dynamic studies became possible is radical **2**. It was

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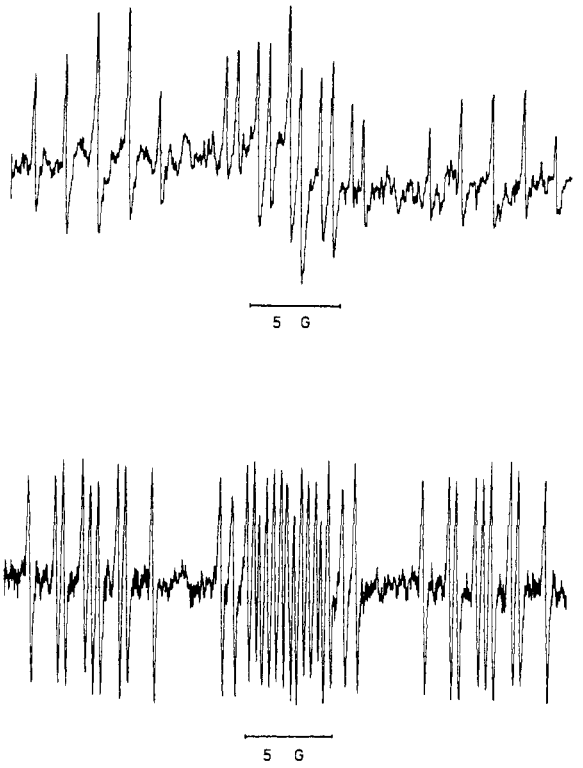
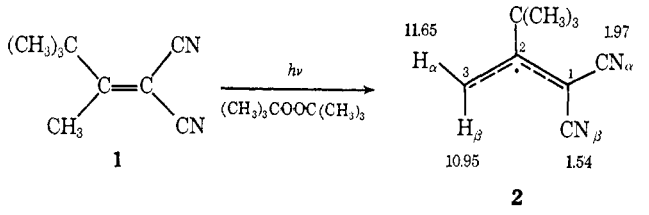


Figure 1. Low temperature esr spectrum (−40°) (bottom) and high temperature spectrum (+69°) (top) of **2**.

generated from **1**[8] on photolysis in the presence of di-*tert*-butyl peroxide[1] and 1,1,1-trichloro-2,2,2-trifluoro-



1 **2**

ethane as solvent. Using a flow system[9] (0.25 cm³ flow/min) and a Philips 1-kW high-pressure mercury lamp, spectra of **2** were recorded on a Varian E3 spectrometer at temperatures from −40 to +69°. The low temperature spectrum together with the high temperature spectrum (fast exchange with an averaged nitrogen coupling constant of 1.75 G) is shown in Figure 1. Rotation is observed about the C_1–C_2 bond. The assignment of nitrogen coupling constants (**2** in gauss) is supported by the 1α-cyano (a_N = 2.30 G) and the 1β-cyano (a_N = 1.91 G) allyl radicals generated from cis and trans crotonitrile by the above procedure. The hydrogen coupling constants for the α_H and β_H positions were assigned according to the known spectra of allyl radicals.[1] No coupling could be resolved for the hydrogen atoms of the *tert*-butyl group.

In the range from −10 to +40° the spectra are temperature dependent. Measurements in this range determining the temperature of the flowing solution at the end of the irradiation zone allows a quantitative

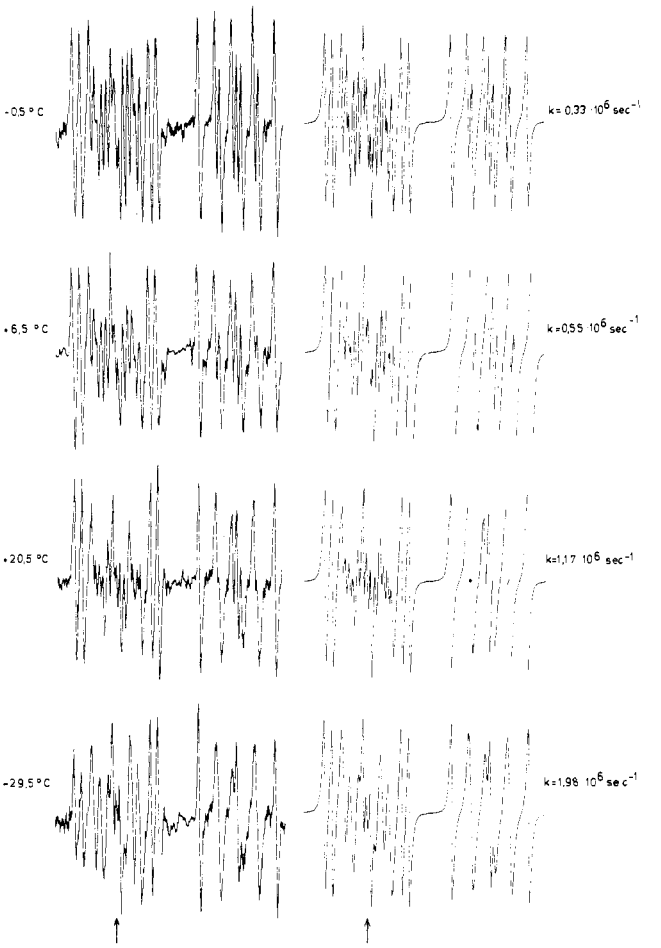


Figure 2. Middle group and right-hand side of esr spectra of **2** at temperatures from −0.5 to +29° (experimental and simulated). The arrows mark the center of the spectra.

analysis. Four experimental and simulated[10] spectra are shown in Figure 2. The data lead to a free energy of activation, $\Delta G^{\ddagger}$ = 9.03 ± 0.06 kcal/mol, which is constant over the temperature range. An error analysis considering an uncertainty of ±2° in the temperature (this is higher than the temperature variation) and taking into account the confidence limits of the rate constants[11] leads to an Arrhenius activation energy of 9.56 ± 0.31 kcal/mol with a frequency factor of 13.18 ± 0.23 and Eyring parameters $\Delta H^{\ddagger}$ = 8.97 ± 0.31 kcal/mol with $\Delta S^{\ddagger}$ = −0.18 ± 1.06 eu.

The magnitude of rotational barriers in allyl radicals can be taken as a measure of allyl resonance. A correction has to be introduced only for the rotational barrier of a bond formed by two sp^2 carbon atoms without π interaction. It seems reasonable that this is of the order of 1 kcal/mol or less as is the case for the sp^2–sp^3 rotational barrier in alkyl radicals.[1,12] The allyl resonance in radical **2** must therefore be in the range of 9–10 kcal/mol. It is smaller by 3–4 kcal/mol than the value for alkyl-substituted allyl systems determined by thermal isomerizations.[5,6] The effect of two cyano groups can be rationalized if stabilization of the ground

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(10) QCPE program 209, submitted by J. Heinzer, ETH Zürich.
(11) We thank Professor G. Binsch, Universität München, for the program to carry out the error analysis according to Demings procedure.
(12) For references see K. S. Chen and J. K. Kochi, *J. Amer. Chem. Soc.*, **96**, 794 (1974).

state of the allyl system as well as of the orthogonal transition state is assumed. The orthogonal transition state consists of a localized radical and therefore the cyano groups should influence its energy to a higher extent than the delocalized ground state.

Presently we are trying to extend our analysis of rotational barriers in allyl systems.

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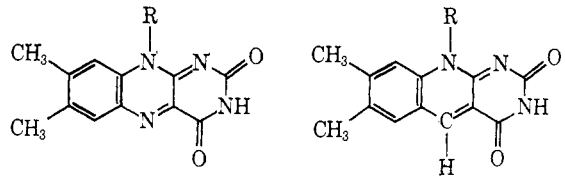
Enzymatic Reduction of 5-Deazariboflavine from Reduced Nicotinamide Adenine Dinucleotide by Direct Hydrogen Transfer

Sir:

Elucidation of the chemical role of the flavine coenzyme remains a compelling question in flavoenzyme oxidative catalysis.[1] Recent studies have suggested proton abstraction and discrete two-electron transfer during enzymatic oxidation of α-hydroxy acids and α-amino acids.[2] Model studies of Bruice and Brüstlein[3] on nicotinamide oxidations have been invoked for hydride transfer in flavoenzyme oxidations of pyridine nucleotides.[4] The ideas of molecular complex formation preceding oxidation[5] and the possibility of covalent adducts between substrates and flavine coenzyme have been recently advanced.[6] With regard to covalent catalysis, Hamilton[6] has favored nucleophilic attack at C_{4a}; others have pointed to N_5 as an electrophilic center on the basis of its reactivity with sulfite,[7] and on theoretical grounds.[8]

The use of 5-deaza analogs (II) of flavine coenzymes (I), R = ribityl for riboflavine (RF) and deazariboflavine (dRF) and R = ribityl-5′P for FMN and dFMN,



I

II

in which a carbon atom replaces nitrogen at position 5 may allow distinction of some of these possibilities especially if they serve as coenzymes. Tollin and colleagues[9] have observed 5-deazaFMN binds to an apoflavoprotein while Bruice, *et al.*, have demonstrated direct hydrogen transfer in model systems between deazaisoalloxazines and either nicotinamides[3] or pyridoxine.[10]

In this communication we report enzymatic evidence that 5-deazariboflavine functions coenzymatically, *undergoing reduction by direct hydrogen transfer* from NADH. We have employed partially purified NADH:FMN oxidoreductase[11] (specific activity = 7.1 U/mg; molecular weight = 24,000 daltons) from *Beneckea harveyi* (formerly *Photobacterium fischeri* strain MAV) which catalyzes reaction 1; unlike most flavoenzymes,

$$\text{NADH} + \text{FMN} + \text{H}^+ \rightleftarrows \text{NAD}^+ + \text{FMNH}_2 \qquad (1)$$

this reduces FMN as a substrate rather than as a tightly bound coenzyme, with the product $FMNH_2$ feeding into the luciferase reaction.[12] We have found that riboflavine can replace FMN in this enzymatic reaction with a K_m of 8.2×10^{-7} M and an equivalent V_{max}. Preliminary tests showed 5-deazariboflavine[13] to be a competitive inhibitor ($K_i = 8. \times 10^{6}$ M) of riboflavine reduction. We then tested the synthetic deazariboflavine, λ_{max} 338 (ϵ 11,000) and 396 nm (ϵ 12,000),[13] for enzyme-catalyzed reduction. Since reduced deazariboflavine reoxidized some 10^4-fold more slowly in air than riboflavine itself ($t_{1/2}$ = 180 min *vs.* <1 sec),[9] it was feasible to monitor loss of absorbance at 396 nm as a direct measure of reaction. We consistently see enzyme-catalyzed reduction of dRF concomitant with NADH oxidation.[14] The rate is 0.3% of the rate observed with riboflavine itself under the given conditions. For an as yet undetermined reason, incomplete reduction of added dRF occurs (*e.g.*, with 1.5 A_{396} units, reduction levels off at about 50% reduction). The nature of this gradual inhibition is apparently not simple accumulation of reduced dRF nor the equlibrium position of the reaction and is under investigation.

As a prelude to testing for enzymatic direct transfer of hydrogen from C_4 of NADH to C_5 of the dRF during reduction, we determined the chirality of transfer to riboflavine itself by measuring ^3H released into water from either 4-(*R*)-[^{3}H]NADH or 4-(*S*)-[^{3}H]NADH.[15]

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(14) Incubation conditions were, in a final volume of 1.0 ml of 0.050 M NaPPi pH 8.6, 125 nmol of dRF, 95 nmol of NADH, and 1.5 units of enzyme. When RF was assayed, 175 nmol of NADH were mixed with 33 nmol of RF.

(15) The 4-(*S*)-[^{3}H]NADH was prepared from 4-[^{3}H]NAD (Amersham–Searle) by reduction with ethanol and yeast alcohol dehydrogenase and the 4-(*R*)-[^{3}H]NADH by incubation of glyceraldehyde 3-phosphate and glyceraldehyde 3-phosphate dehydrogenase in the presence of arsenate.