very close to the CD curve for pure L-tryptophan. For comparison, the CD for the entire mixture is also shown.

These encouraging results on mixtures have led us to extend our experiments to macromolecules. Thus far we have measured the FDCD spectra of lysozyme and t-RNA^{Phe}. Here the fluorescent chromophores are the tryptophans and the anticodon loop Y base, respectively.[7,8] The signal-to-noise ratios in both spectra are several times larger than for the mixtures reported above. This is reasonable since the CD of free L-tryptophan is rather small relative to the CD of a residue in a protein or nucleic acid. To analyze these data, it will be necessary to obtain a value of ϵ_F for the chromophore in its macromolecular environment. There are several possible ways to accomplish this, including measurement of the corrected excitation spectra of the solutions.

The FDCD technique makes it possible to measure the CD of only the fluorescent chromophores in a macromolecule, provided there is little or no energy transfer. This greatly enhanced specificity for CD measurements is very difficult, if not impossible, to obtain by other methods.[9] Unique structural information on selected regions of biologically important macromolecules may thus be obtained.

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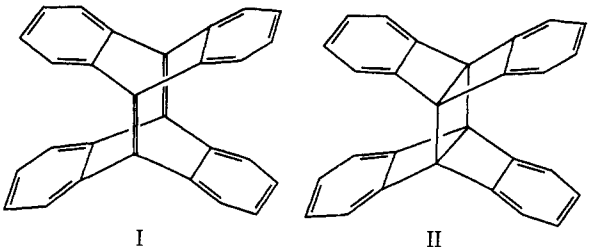
9,9′,10,10′-Tetradehydrodianthracene. Formation, Protection, and Regeneration of a Strained Double Bond

Sir:

We wish to report the synthesis, characterization, and X-ray analysis of a novel, highly strained diene, 9,9′,10,-10′-tetradehydrodianthracene (I).[1]

Previously, we have described the strained olefin IV, 9,9′-didehydrodianthracene.[2,3] The isolation of this compound interested us in the possibility of synthesis of the tetradehydro compound and in the question of whether such a compound would exist as the diene I and/or the propellane II or conceivably some structure

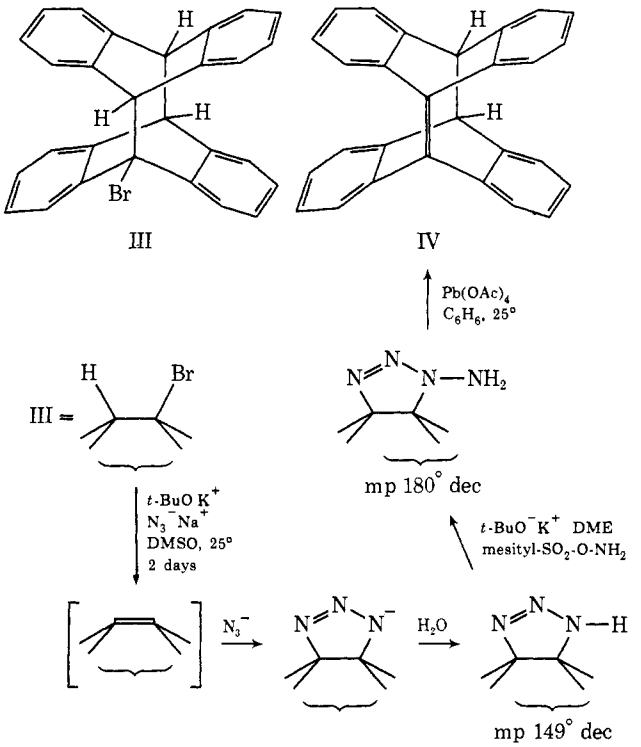


I II

intermediate between the two.

The approach taken to the synthesis was to devise a way for the formation, protection, and subsequent regeneration of a highly reactive bridgehead double bond. A successful sequence (and a new synthesis for 9,9′-didehydrodianthracene (IV)) is shown in Chart I: dehydrohalogenation of 9-bromodianthracene (the product of cross dimerization of 9-bromoanthracene and anthracene)[4] to the bridgehead olefin and capture of the olefin by azide ion (in the absence of azide, the base adds to the olefin); conversion of the triazoline[5,6] to the N-aminotriazoline[6] by Carpino's reagent, hydroxylamine O-mesitylenesulfonate;[7] oxidation of the N-amino derivative with lead tetraacetate.[8]

Chart I



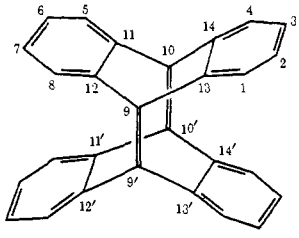
(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research.
(2) N. M. Weinshenker and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 506 (1968).
(3) According to IUPAC, Nomenclature of Organic Chemistry, Rule C − 41.2, loss of two hydrogens from a compound is denoted by the prefix "didehydro." In common usage "dehydro" is often used in place of "didehydro" (*e.g.*, benzyne is called "dehydrobenzene"). Compound IV was originally called "dehydrodianthracene (ref 2); however, we think that confusion will be minimized by calling compound IV 9,9′-didehydrodianthracene and compound I 9,9′,10,10′-tetradehydrodianthracene (also known as the Viavattene–Greene Diene). A more complete name is 3,4:7,8:9,10:11,12-tetrabenzotricyclo[4.2.2.2^{2,5}]dodeca-1,3,5,7,9,11-hexaene.
(4) D. E. Applequist, R. L. Litle, E. C. Friedrich, and R. E. Wall, *J. Amer. Chem. Soc.*, 81, 452 (1959).
(5) Reaction of the triazoline anion with trimethyloxonium fluoroborate afforded the N-methyltriazoline, identical with the product of addition of methyl azide to olefin IV, mp 234–235° dec; analysis for C, H, and N was satisfactory.
(6) The free triazoline and N-aminotriazoline are thermally unstable and acid sensitive.
(7) L. A. Carpino, *J. Amer. Chem. Soc.*, 82, 3133 (1960).
(8) The latter two steps of the synthetic sequence parallel a benzyne synthesis of C. D. Campbell and C. W. Rees, *J. Chem. Soc. C*, 742, 748, 752 (1969).

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



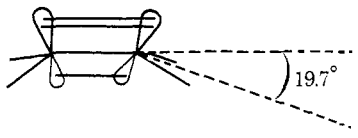
I

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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(5) W. v. E. Doering and G. H. Beasley, *Tetrahedron*, **29**, 2231 (1973), and references cited therein.

(6) W. R. Roth, G. Ruf, and P. W. Ford, *Chem. Ber.*, **107**, 48 (1974).

(7) H. Trill, Dissertation, Universität Münster, 1974.