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Stuart W. Staley,* Marye Anne Fox
Department of Chemistry, University of Maryland
College Park, Maryland 20742

Allan Cairncross*
Contribution No. 2452 from Central Research and
Development Department
Experimental Station, E.I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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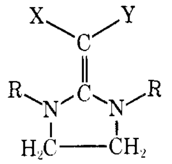
Demonstration of Fourfold Rotational Barriers in Push-Pull Ethylenes

Sir:



1, X = PhCO; Y = $COCH_3$; R = CH_2Ph
2, X = p-BrC_6H_4CO; Y = CN; R = CH_3
3, X = Ph; Y = CN; R = CH_2Ph
4, X = Ph; Y = CN; R = CH_3
5, X = p-$NO_2C_6H_4$; Y = CN; R = CH_2Ph

The barrier to rotation around the carbon-carbon double bond in ethylenes with strong donor groups on one carbon atom and strong acceptors on the other may be quite low owing to a superior stabilization of the zwitterionic transition state.[1-3] When this effect is combined with a strong steric interaction between the donor and acceptor groups, permanently twisted ethylenes result.[4,5] An example is found in **1**, where a free-energy barrier to passage through the planar state of 16.9 kcal/mol has been evaluated by bandshape analysis of the AB spectrum of the benzylic protons.[6] The x-ray crystallographic structure of **2**[5] shows nearly planar CO-C-CN and imidazolidine parts with a dihedral angle between these planes of 41°. For these molecules the relation between the potential energy and the dihedral angle (θ) may have a high "steric barrier" at $\theta = 0$ and 180° and a lower barrier caused by loss of π-electron interaction across the double bond (the π-electron barrier)[4] at 90 and 270°. It is evident that the steric as well as the π-electron barrier have important contributions from both kinds of energy.

The benzylic protons in compounds like **1** with strong acceptor groups show only one AB spectrum down to −140 °C, *i.e.*, their π-electron barriers are too low to be measured. In **3** on the other hand, the benzylic proton resonance shows no AB spectrum in the accessible temperature region but only a symmetrical doublet below −94 °C, showing that the π-electron barrier is 8.5 kcal/mol but that the steric barrier is too low to be measured. In **4** the π-electron barrier is 9.5 kcal/mol,[7] and the barrier difference between this molecule and **3** is probably due to increased ground-state strain caused by the benzyl groups. In **5**, the nitro group lowers the π-electron barrier and only a singlet benzylic proton resonance is observed above −140 °C.

In **6**, the increased ring size raises the steric barrier, and it can be measured by DNMR technique. An AB spectrum appears below −54 °C, corresponding to a steric barrier of 10.7 kcal/mol. Below −90 °C first the high-field part and then also the low-field part of the AB spectrum undergo selective broadening. At −130 °C new very broad signals have emerged, and at this and higher temperatures the spectrum can be satisfactorily simulated by use of the DNMR-3 program,[8] assuming exchange between two AB systems.[9] From the rate constants a π-electron barrier of 7.0 kcal/mol can be derived. An analogous barrier in **7** gives rise to a decoalescence of the

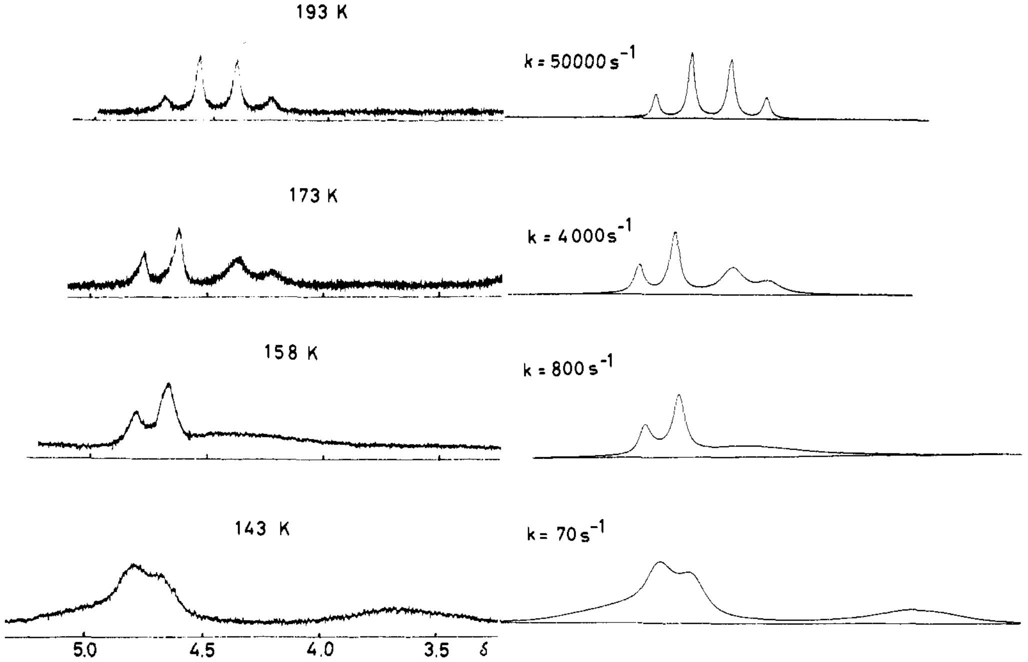
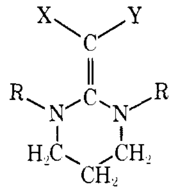


Figure 1. Experimental (100 MHz) and calculated spectra of the benzylic methylene protons of **6**. Chemical shifts: A_1, δ 4.67; A_2, δ 4.58; B_1, δ 3.57; B_2, δ 4.94. T_2 (from top to bottom): 0.10, 0.07, 0.05 and 0.03 s.



6, X = Ph; Y = CN; R = CH_2Ph
7, X = Ph; Y = CN; R = CH_3
8, X = p-$NO_2C_6H_4$; Y = CN; R = CH_2Ph
9, X = p-$NH_2C_6H_4$; Y = CN; R = CH_2Ph

N-methyl resonance at −125 °C ($\Delta G^{\ddagger}$ = 7.4 kcal/mol). The low π-electron barriers in the six-membered compounds are at least partly due to increased ground-state strain, but improved stabilization of the zwitterionic transition state may also contribute.

Models and simple strain-energy calculations indicate that the aryl group must be nearly orthogonal to the double bond on passage over the steric barrier, and the para substituent must influence this barrier by the loss of conjugation in the transition state. Thus the steric barrier in **8** is considerably raised ($\Delta G^{\ddagger}$ = 13.9 kcal/mol) whereas no π-electron barrier can be measured. In **9**, on the other hand, the π-electron barrier is raised and the steric barrier is lowered compared to **6**. The rotations past the two barriers now occur with similar rates, and the exchange system is quite complex. Precise rate constants could therefore not be evaluated but an approximate steric barrier of 9.5 kcal/mol (T_c ca. −75 °C) could be calculated.

It might be argued that the AB spectra given by **6**, **8**, and **9** could be caused by pyramidal ring nitrogen atoms exhibiting slow inversion rather than by twisted double bonds. Against this interpretation speaks the x-ray structure[5] and also the observation that the ring N-CH_2 resonances in **6** and **8** appear as sharp triplets throughout the region of broadening of the benzylic proton resonances.

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Jan Sandström,* Ulf Sjöstrand, Ingegerd Wennerbeck
Division of Organic Chemistry 1, Chemical Center
P.O.B. 740 S-220 07 Lund 7, Sweden

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A Water-Stable Cu(III) Complex

Sir:

The ability of cupric salts to form intensely colored products in the presence of oxalodihydrazide and certain aldehydes and ketones was first noted by Nilsson[1] and developed into a sensitive analytical method for copper by Gran and coworkers.[2,3] Frieden et al.[4] recognized that the intense color was produced only in the presence of molecular oxygen and proposed that these copper complexes might serve as good models for "blue" copper proteins[5] as well as the oxygen-transport protein, hemocyanin.[6] In an effort to determine whether an oxygenation process is indeed responsible for the intense coloration of the copper-bis(oxalodihydrazide) system, Clark and coworkers[7] solved the crystal structure of the violet complex formed with acetaldehyde. The copper is coordinated to a macrocyclic ligand formed by condensation reactions between 6 mol of acetaldehyde and 2 mol of oxalodihydrazide, but a liganded oxygen molecule is clearly not present (Figure 1). No systematic chemical and spectroscopic characterizations of these complexes have heretofore been published. In this paper, we demonstrate that oxygen and other oxidizing agents convert copper to the trivalent state and that it is a Cu(III) complex which is responsible for the unusually high absorptivity (ϵ_{540} = 29 500 M^{-1} cm^{-1})[2,7] in this system.

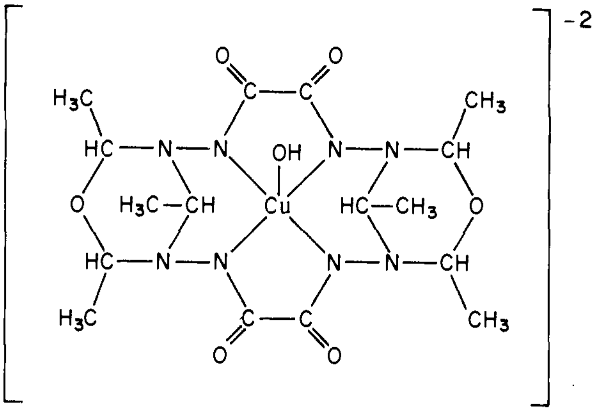

Figure 1. Disodium *bcde*-[7,9,16,18,19,20-hexamethyl-8,17-dioxa-1,2,5,6,10,11,14,15-octaazatricyclo[13.3.$1^{6,10}$]eicosane-3,4,12,13-tetronato(4−)-N^2,N^5,N^{11},N^{14}]-a-hydroxocuprate(III), hereafter designated [Cu(III) macrocycle], based on the x-ray crystallographic study of Clark et al.[7] and this work.

Under anaerobic conditions, oxalodihydrazide (0.59 g, 5.0 mmol) was added to a solution of copper(II) sulfate pentahydrate (0.25 g, 1.0 mmol) in 20 mL of water. Ammonium hydroxide (3 mL, 45 mmol) was added with stirring, and, after all of the oxalodihydrazide had dissolved, acetaldehyde (3 mL, 50 mmol) was added. Upon shaking in air, the solution became intensely violet. This was filtered, applied to a Bio-Rad AG 1-X8 anion-exchange column (6.5 × 85 cm, 100-200 mesh, 4.1-equiv capacity, Cl^-/OH^- form) and eluted (0.5 mL/min) with 0.02 M NaCl adjusted to pH 8 with NaOH. The mixture separated into three components, one light band followed by two very intensely colored bands. The visible absorption spectrum of the middle band was identical with that of the compound reported by Clark et al.[7] This band was collected, freeze-dried, dissolved in a minimum amount of water at pH 8, and passed down a column containing Sephadex G-15 (5 × 100 cm, 650-g dry wt). The violet band was collected and freeze-dried. Anal. Calcd. for $Na_2C_{16}H_{25}CuN_8O_7 \cdot 8H_2O$): C, 27.64; H, 5.96; N, 16.12; Cu, 9.14; found: C, 26.55; H, 5.10; N, 17.13; Cu, 7.81. Similar to Clark et al.,[7] we have not been able to obtain good elemental analyses and our crystallization attempts have thus far been unsatisfactory. The violet compound, however, migrates as a single component in both TLC and electrophoresis at pH 8. Upon lowering the pH, the UV-vis spectrum (Figure 2) changes isosbestically (p$K_a \simeq$ 5) with a concomitant decrease in the electrophoretic mobility, which is consistent with protonation of the original dinegative anion. The ^1H NMR spectrum (Figure 3) consists of two quartets and two doublets of relative areas 1:2:6:3, thus accounting for all of the proton resonances expected from the structure shown in Figure 1.