more repulsive the $5s^1$ state the greater the chance of such a curve crossing. The monoligand complexes in Table I show uniformly smaller E_R values than their diligand counterparts. This can be attributed to the involvement of the $5p_x$ orbital in the monoligand geometry, which, through hybridization, can moderate the repulsiveness of the 5s orbital in its interaction with the occupied π_x MO of the ligand. On the other hand, the stability of the $5p_y^1$ state will strongly depend on the Ag $5p_y$–ligand π_x^* interaction, which should increase as δ decreases. Analogously, the repulsiveness of the $5s^1$ state will increase as the Ag 5s–ligand π_x energy gap decreases. Thus, for example substitution of Ag by Cu, which has slightly more stable $(n + 1)$s and $(n + 1)$p atomic orbitals,[7] should decrease the $(n + 1)$s–π_x energy differences and enhance the possibility of isolating the $(n + 1)p_y^1$ complex. Substitution of the ligand hydrogen atoms with electron-releasing groups such as alkyl (steric effects aside) should have a similar effect. Substituting Cu for Ag will also give a diacetylene complex with a smaller nd_{xz}–π_z repulsive interaction because of the 60% smaller radius of the Cu 3d atomic orbital.[8] For all these complexes, π_x is expected to be stabilized by a reduction in interaction with the metal nd atomic orbital. In fact, Kasai has reported[1] that copper atoms form both ML_2 and ML symmetric complexes with ethylene and acetylene.

Finally, it should be noted that the set of low-lying electronic states described here for the silver–ligand systems is very similar to that found in the rare gas halide and oxide electronic transition lasers which give rise to the familiar "bound–free" laser emission process.[9,10]

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syn-1,6:8,13-Diimino[14]annulene

E. Vogel,* F. Kuebart, J. A. Marco, and R. Andree

Institut für Organische Chemie der Universität zu Köln
D-5000 Köln 41, West Germany

H. Günther* and R. Aydin

Universität GH Siegen, FB 8
D-5900 Siegen 21, West Germany

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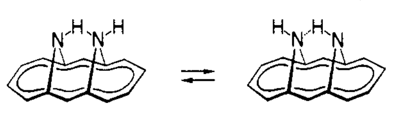
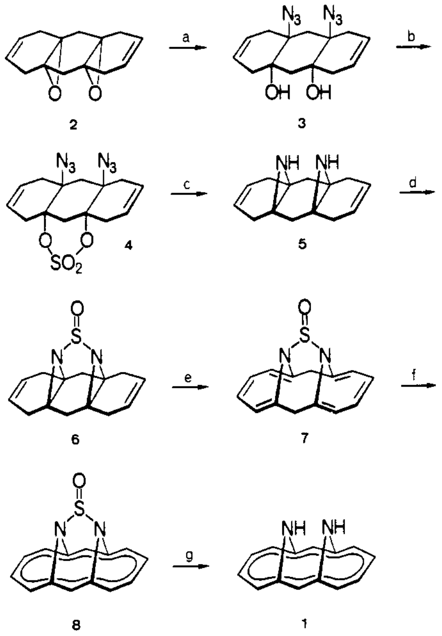
The heretofore elusive *syn*-1,6:8,13-diimino[14]annulene (**1**)[1] features two closely spaced NH groups that are anticipated to have the hydrogens in the exo,endo position [**1a**/**1b**] due to sterically promoted hydrogen bonding. One of the most intriguing aspects of **1** is the possible occurrence of two rather unprecedented degenerate dynamic processes involving the proximate NH groups: (1) a "windshield wiper" flip of the NH protons, tantamount to a tandem configurational inversion of the two nitrogen atoms [**1a** ⇄ **1b**] and (2) an inversion of the two NH bridges through the plane of the [14]annulene ring. While the former process should be detectable by NMR spectroscopy, the latter one might be amenable to examination using chirality of an appropriately substituted 1,6:8,13-diimino[14]annulene as a probe.[2]



1a 1b

Scheme I



^{a} NaN_3 (5 equiv), $MgCl_2 \cdot 6H_2O$, MeOH, reflux, 72 h (64%). ^{b} Oleum (65% SO_3) (4 equiv), Et_2O, −45 °C, then stirring at room temperature, 12 h (56%). ^{c} $LiAlH_4$ (2.2 equiv), THF, −25 °C, then stirring at 0 °C, 12 h (75%). ^{d} $SOCl_2$, Et_3N (2 equiv), Et_2O, 0 °C, then room temperature, 12 h (65%). ^{e} Br_2 (2 equiv), CH_2Cl_2, −78 °C; DBN (6 equiv), THF, −10 °C, 2 h, then room temperature, 24 h (35% from **6**). ^{f} DDQ (1.1 equiv), benzene, reflux, 2 h (75%). ^{g} HOAc/1 N HCl (1:1), 80 °C, 30 min (65%).

After previous unsuccessful approaches toward its synthesis, **1** has now been prepared following a hexahydroanthracene route (Scheme I).

1,4,5,8,9,10-Hexahydroanthracene,[3] when epoxidized with 40% peracetic acid, regioselectively afforded **2** and its anti isomer as a 6:4 mixture (95%) from which **2** (mp 187–189 °C, dec; 45%) was separated by chromatography on silica gel (dichloromethane/ethyl acetate).[4] Interestingly, **2** on treatment with sodium azide in methanol in the presence of magnesium chloride[5] experienced regioselective opening of the two epoxide rings to give as the only product the diazido diol **3** (mp 201–202 °C dec; 64%),[6] whereas the anti isomer reacted only sluggishly under these conditions yielding ill-defined products. This reactivity pattern obviated the tedious separation of the *syn-anti*-bis(epoxide) mixture. At the stage of **3**, the synthesis of **1** was stymied for quite some time, since this intermediate defied all attempts at acylation to convert its hydroxy functions into leaving groups. Even such powerful acylating agents as triflic anhydride or sulfuryl chloride (entropy-assisted formation of the cyclic sulfate **4**) left **3** virtually unaffected.

Finally, the desperate experiment of reacting **3** with oleum (ca. 65% SO_3)[7] in ether met with success in that it afforded **4** as the

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(1) Bridged [14]annulenes with an anthracene perimeter are already known in great structural variety. For reviews see: (a) Vogel, E. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1968**, *12*, 215–251; (b) *Pure Appl. Chem.* **1969**, *20*, 237–262; (c) *Ibid.* **1971**, *28*, 355–377; (d) *Isr. J. Chem.* **1980**, *20*, 215–224; (e) *Pure Appl. Chem.* **1982**, *54*, 1015–1039. (f) Nozaki, H., Ed. "Current Trends in Organic Synthesis": Pergamon Press: Oxford and New York, 1983; pp 379–400.

(2) An inversion of this type has recently been detected in the *syn*-1,6:8,13-diepoxy[14]annulene system by employment of optically active 2,9-dibromo-*syn*-1,6:8,13-diepoxy[14]annulene, private communication by Prof. K. Schlögl, University of Vienna, Austria.

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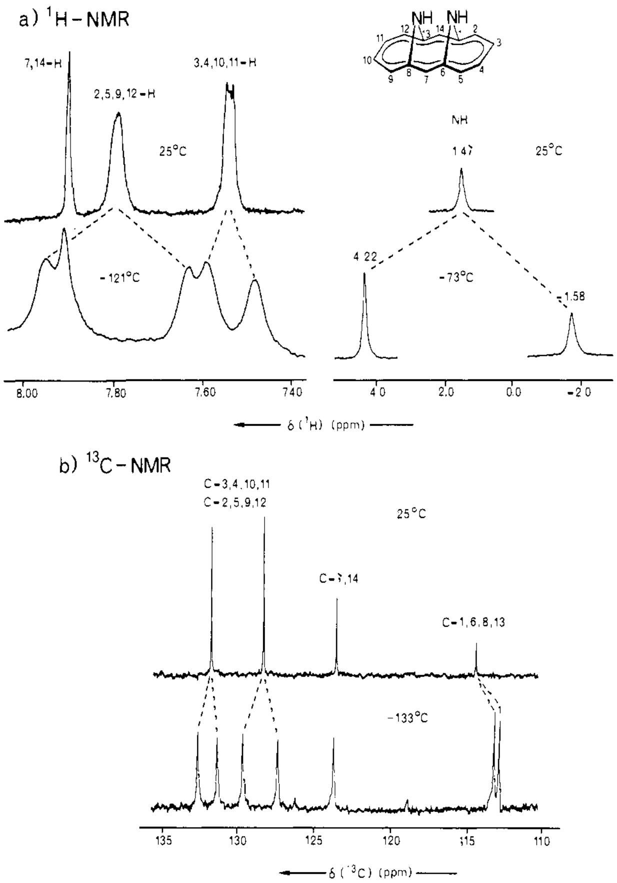

Figure 1. (a) 400-MHz ^{1}H NMR (25 °C, 0.2 M in $CDCl_3/CCl_4$ 10:1; low temperature, 0.1 M in CD_2Cl_2/C_2H_5Cl 2:1); (b) 100-MHz ^{1}H-decoupled ^{13}C NMR (25 °C, 0.07 M in CD_2Cl_2; −133 °C, 0.1 M in CD_2Cl_2/C_2H_5Cl 2:1).

sole isolable product (mp 170 °C, dec; 56%). As anticipated, reduction of **4** with lithium aluminum hydride furnished **5** (mp 83 °C; 75%). When **5** was treated sequentially with bromine in dichloromethane and sodium methoxide in THF, 7,14-dihydro-*syn*-1, 6:8,13-diimino[14]annulene (mp 145 °C), a bis(1*H*-azepine), was obtained[8] but the dehydrogenation of this chemically capricious molecule led to complex mixtures of products. In order to avoid the intermediacy of the 7,14-dihydro derivative of **1**, the bis(aziridine) **5** was protected as its sulfinamide **6** (mp 204–205 °C; 65%). Application of the bromination–dehydrobromination reaction sequence to **6** provided **7**, which after isolation by chromatography was treated with 2,3-dichloro-5,6-dicyanobenzoquinone to give **8** [26%, based on **6**]. The protection method employed with **5** served admirably, since **1** was smoothly liberated from **8** by acid hydrolysis. After crystallization from benzene, **1** was obtained as air-stable scarlet red prismatic crystals [mp 158 °C; 65%; UV (methanol) 305 (ϵ 105 700), 340 sh (12 400), 376 (8400), 532 nm (700); IR (CsI) 3170, 3038, 1531 cm^{-1}; as determined spectrophotometrically, **1** behaves as a monoamine toward perchloric acid exhibiting a pK_a of 5.74].[9]

The structure and dynamic behavior of **1** follow from NMR spectroscopic studies. In the ^{1}H NMR spectrum at room temperature, the annulene protons give rise to a singlet at δ 7.89 (H-7,14) and an AA′BB′ system at δ 7.80 (H-2,5,9,12) and 7.53 (H-3,4,10,11) (J_{23} = 8.86, J_{34} = 9.62 Hz), whereas the NH protons appear as a broadened singlet at δ 1.47 (Figure 1a). As indicated by both the chemical shifts and the coupling constants, **1** must possess a delocalized π-electron system.[10] Dynamic behavior of **1** is revealed by the reduced spectral symmetry on lowering the temperature: at −100 °C two AA′BB′ systems and two NH signals [δ 4.22 (H_{endo}) and −1.58 (H_{exo})] occur. Correspondingly, the four signals observed in the ^{13}C NMR spectrum at room temperature [δ 114.21 (C-1,6,8,13), 128.42 (C-2,5,9,12), 131.90 (C-3,4,10,11), 123.55 (C-7,14)] increase to seven in the slow exchange limit at −133 °C (Figure 1b). Evidence that the dynamic process in question is the configurational inversion of the nitrogen atoms (**1a** $\rightleftarrows$ **1b**) is provided by the following findings: (1) the ^{1}H and ^{13}C NMR signals of H-7,14 and C-7,14, respectively, remain unaffected as the temperature is decreased; (2) in hydrogen-bonding solvents such as CH_3OD the coalescence temperature, and hence the barrier of the process, is raised; (3) the occurrence of a π-bond shift, while being compatible with the changes in the ^{13}C NMR spectrum, is ruled out by the characteristic features in the ^{1}H NMR spectrum.[11] A line shape analysis of the three two-site exchange systems encountered in the ^{13}C NMR spectrum afforded $\Delta H^{\ddagger}$ = 26.1 kJ mol^{-1} and $\Delta S^{\ddagger}$ = −76.5 J mol^{-1} K^{-1} for the inversion of the nitrogen atoms (**1a**) $\rightleftarrows$ (**1b**), which is assumed to be synchronous.[12] The intramolecular nature of this inversion derives from the observation that the rate constants are not dependent on concentration within experimental error.[13]

Acknowledgment. J. A. Marco thanks the Alexander von Humboldt-Foundation for a fellowship.

Registry No. 1, 75863-17-1; *syn*-**2**, 10133-47-8; *anti*-**2**, 5910-29-2; **3**, 87533-11-7; **4**, 87533-12-8; **5**, 87533-13-9; **6**, 87533-14-0; **7**, 87533-15-1; **8**, 87533-16-2; 1,4,5,8,9,10-hexahydroanthracene, 5910-28-1; 7,14-dihydro-*syn*-1,6:8,13-diimino[14]annulene, 87533-17-3.

Supplementary Material Available: NMR, IR, and UV spectral data of intermediates **2–8** (1 page). Ordering information is given on any current masthead page.

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(11) The ^{1}H NMR chemical shifts and coupling constants of **1** match those of the nondynamic *syn*-1,6:8,13-diepoxy[14]annulene, which has been shown by X-ray analysis to possess a delocalized 14π-electron system.

(12) The existence of high-energy exo,exo (lone-pair repulsion) and/or endo,endo isomers (H,H repulsion) as intermediates cannot be excluded.

(13) At 200, 210, 215, 217, and 221 K the following rate constants were obtained for a 0.1 and 0.05 M solution of **1** in CD_2Cl_2/C_2H_5Cl (7:3), respectively: k (s^{-1}) 53/38, 124/105, 182/199, 228/227, 308/295.

ESR Study of Twisting in Trimethylsilyl-Substituted Alkene Cation Radicals[1]

Mitsuo Kira, Hiroko Nakazawa, and Hideki Sakurai*

Department of Chemistry, Tohoku University
Sendai 980, Japan

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A number of theoretical studies predicted substantial twisting from planarity in alkene cation radicals.[2] For instance, recent MNDO-UHF calculations[2f] have shown 25° twist in the ethene cation radical and a much larger twist angle in the tetramethyl derivative. Several spectral analyses confirmed such a twisting in the ethene cation radical.[3] Although ESR is a powerful tool for investigating the electronic structure and geometry of radical

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