Ru(1)–N(3) is 1.928 (6) Å. The N–N distance is 1.124 (15) Å, only slightly longer than that in free N_2 (1.0976 Å)[4] or N_2^+ (1.118 Å),[5] and well below the N–N distance in hydrazine (1.46 Å).[6] Five ammonia groups complete the octahedral coordination about each ruthenium, with the two equatorial sets in an eclipsed conformation (as required by symmetry). The apical N(9)–Ru(1) distance is 2.140 (6) Å, which is slightly longer than the average equatorial nitrogen–ruthenium bond length of 2.12 Å. One of the two BF_4^- groups in the asymmetric unit is either disordered or undergoing large thermal motion, so that accurate atomic positions could not be obtained. The other BF_4^- group is tetrahedral; the mean B–F distance is 1.34 Å.

The structure of the cation is in complete accord with infrared spectral results which show[1] only a very weak band in the 2050–2100-cm^{-1} region. In addition, recent Raman data have corroborated the linear nature of the Ru—N≡N—Ru unit.[7]

A preliminary model of the electronic structure of $Ru_2(NH_3)_{10}N_2^{4+}$ may be proposed for idealized D_{4h} symmetry; assuming that the important Ru–N_2 bonding involves the π^*N_2 level, we propose the molecular orbital ordering e_g $(xz_1 + xz_2, yz_1 + yz_2) < b_{2g}$ $(xy_1 + xy_2) \sim b_{1u}$ $(xy_1 - xy_2) < e_u$ $(xz_1 - xz_2, yz_1 - yz_2) < e_g(\pi^*N_2)$. In this formulation, the ground state is $(e_g)^4(b_{2g})^2(b_{1u})^2(e_u)^4 \equiv {}^1A_{1g}$. The π bonding from the two Ru centers to the N_2 is provided by the four electrons in the e_g level, giving an average of one π bond per Ru. In the reference mononuclear complex, $Ru(NH_3)_5N_2^{2+}$, which is known to have a linear RuN_2 unit,[8] the π-bond order is two and a somewhat shorter Ru–(N_2) distance would be expected. Although accurate molecular parameters are not yet available for $Ru(NH_3)_5N_2^{2+}$, the fact that $[Co(H)(N_2)(PPh_3)_3]$ shows[9] a metal–N_2 bond length of 1.8 Å may be taken as evidence that the π interactions per metal center have decreased in $Ru_2(NH_3)_{10}N_2^{4+}$. It is also interesting to note that the N–N distances in the two structures are not significantly different (1.11 Å in Co^I—N≡N,[9] 1.124 (15) Å in Ru^{II}—N≡N—Ru^{II}); again this observation is in accord with the crude theory because both mononuclear and binuclear systems furnish a *total* of four $d\pi$ electrons to the π^*N_2 level.

The intense absorption band at 263 nm (ϵ 4.8 × 10^4) which characterizes[1] the $Ru_2(NH_3)_{10}N_2^{4+}$ complex may be assigned to the allowed metal-to-ligand charge-transfer transition $e_u \rightarrow e_g$ (π^*N_2). The model allows a qualitative understanding of the much higher energy of the $Ru \rightarrow \pi^*N_2$ band in $Ru(NH_3)_5N_2^{2+}$. (The intense band is found[10] at 221 nm in the latter complex, which is *ca.* 7200 cm^{-1} higher than in the binuclear case.) The occupied d levels should be at relatively lower energy in $Ru(NH_3)_5N_2^{2+}$, because the partial withdrawal of four $d\pi$ electrons through $d\pi \rightarrow \pi^*N_2$ bonding leaves the central ruthenium with a larger effective positive charge than in the binuclear case. Thus, excitation of either a metal b_2 or e electron to $e(\pi^*N_2)$ in the C_{4v} mononuclear complex would require more energy than the $e_u \rightarrow e_g(\pi^*N_2)$ transition in $Ru_2(NH_3)_{10}N_2^{4+}$.

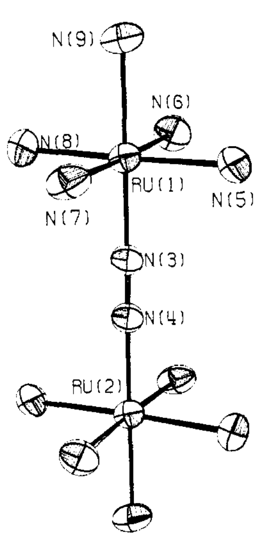

Figure 1. A view of the $Ru_2(NH_3)_{10}N_2^{4+}$ cation. The atoms are represented by ellipsoids whose principal axes were derived from the final values of the anisotropic temperature parameters.

We conclude that a simple molecular orbital model which emphasizes the importance of $Ru \rightarrow \pi^*N_2$ π bonding is adequate as a basis for discussion of relevant bond parameters and the electronic spectra of $Ru_2(NH_3)_{10}N_2^{4+}$ and $Ru(NH_3)_5N_2^{2+}$.

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Photochromism of 1,2-Dihydroquinolines

Sir:

As a part of our continuing investigation of the spectroscopy and primary photochemical processes of molecules,[1] we wish to report photochemistry (photochromism) of the 1,2-dihydroquinolines. Their colorless solid solutions in EPA[2] at −196° develop color upon irradiation with ultraviolet light (1-kW Hg–Xe source, Corning glass filter 9863 transmitting approximately in the region of 250–390 nm).

The colored form can be eradicated thermally and the process can be repeated several times. Thus far, we have investigated six dihydroquinolines; five of them exhibited photochromic behavior. They are listed in Table I.[3]

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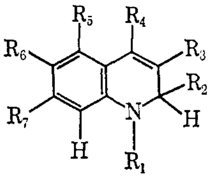
(1) For example, see R. S. Becker and J. Kolc, *J. Phys. Chem.*, **72**, 997 (1968), and references therein; A. Santiago and R. S. Becker, *J. Amer. Chem. Soc.*, **90**, 3654 (1968); R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, **50**, 239 (1969), and references therein.

(2) Ethyl ether, isopentane, and ethyl alcohol in volume ratio of 5:5:2, respectively.

(3) Compound **1** was synthesized in this laboratory according to H. Rupe, R. Paltzer, and K. Engel, *Helv. Chim. Acta*, **20**, 209 (1937), and recrystallized several times from ethanol. Compounds **3** and **4** were purchased from Aldrich Chemical Co.; compounds **2** and **5** (and also **1**) were generously donated by Dr. F. D. Popp, Clarkson College of Technology, Potsdam, N. Y. Compound **6** was a kind gift from Drs. H. O. Huisman and W. N. Speckamp, University of Amsterdam, The Netherlands.

Table I



Compound no.	R1	R2	R3	R4	R5	R6	R7	Colored form in EPA matrix at 77°K
1	COC_6H_5	CN	H	H	H	H	H	Brownish red
2	$CO_2C_2H_5$	CN	H	H	H	H	H	Orange
3	$CO_2C_2H_5$	OC_2H_5	H	H	H	H	H	Pink
4	CN	OH	H	H	H	H	H	Blue
5	COC_6H_5	CN	H	H	Benzo		H	Yellow
6	$SO_2C_6H_4CH_3$	H	CN	OCH_3	H	H	OCH_3	None

Compound **3** was subjected to the three irradiation–thermal eradication cycles. The total reversibility after the three cycles was better than 99% as determined by monitoring the absorption of the uncolored form in the region 280–310 nm. Similarly, compounds **1** and **5** were cycled five times with the complete disappearance of the visible band after each cycle. Reversibility was 97–98% per cycle. In the cases the of compounds **1** and **5**, there is some side reaction in addition to the reversible photochromic process. This is responsible for the gradual development of an additional band with an onset in the 370–400-nm region. The reversibility of compounds **2** and **4** was considerably lower than those considered above.

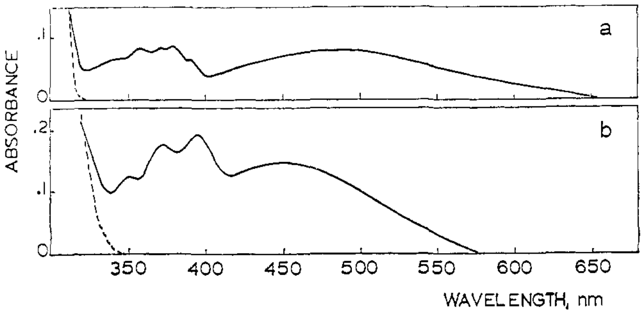
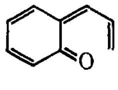


Figure 1. Absorption spectra of colored forms (——) of: (a) 1-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (1.2×10^{-3} M at 20° in EPA); (b) 1-benzoyl-2-cyano-1,2-dihydroquinoline (5.7×10^{-4} M at 20° in EPA). All spectra were taken in 2-mm Suprasil cells at −196°, irradiated 20 min with 1-kW Hg-Xe source at −196°; colorless forms before irradiation, - - - -.

The colored forms of dihydroquinolines **2** and **5** persist upon melting of the EPA matrix and warming up to room temperature, at which temperature they stay for some time. Some of the compounds (*e.g.*, **1**, **2**, and **5**) can be converted to their colored forms in liquid solution at −75°, and compound **2** at temperatures above 0°. Photochromism of the 1,2-dihydroquinolines seems to depend strongly upon the presence and nature of the substituents in positions 1 and 2; see Table I. Thus, compound **6** is not convertible to a colored form, and its first absorption band stays virtually unchanged upon prolonged irradiation. This effect of substituents is being studied further.

Absorption spectra of the colored forms of all compounds investigated show a broad band in the visible region and a more intense, usually structured band in the region 320–400 nm. Examples are given in Figure 1. A striking similarity exists with the absorption spectra of the colored forms of chromenes;[4] we have shown the structure of the colored form[5] to be **7**. This



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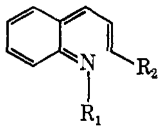

8

indicates the strong possibility of a parallel structure **8** for the colored form of the 1,2-dihydroquinolines. A more detailed investigation of the photochemistry and spectroscopy of the dihydroquinolines is in progress.

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Solvent Effects on Molecular Complex Formation. Pyridine–Iodine System

Sir:

Recently, results were presented showing the influence of nonpolar solvents on the pyridine–iodine complex formation reaction.[1] The variation of the 1:1 complex formation constant (K_c, in liters/mole units) was related to the solubility parameters of the solvents (δ_s) by the expression proposed by Buchowski, *et al.*[2]

$$\log K_c = a + b\delta_s \qquad (1)$$

in which a and b are parameters depending only on the properties of the donor (D) and acceptor (A). An alternative method has also been developed for predicting the effect of solvation on complex formation

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