the II dimers and recovered xanthene both indicated, by nmr, *ca.* 50% monodeuteration of II and of xanthene. These data suggest that the pK_a is near that of xanthene (~29).

We have directly determined the pK_a of cyclopentadiene in this medium relative to *t*-butyl alcohol (pK_a = 19.0)[7] by observing the intensity of the nmr spectrum of cyclopentadienyl anion as a function of *t*-butyl alcohol. From the relative concentration of *t*-butyl alcohol required to reduce the signal of the anion to half-height, the pK_a of cyclopentadiene is 18.2 ± 0.2 in the medium at 35°.

Thus the effect of the fused cyclobutadiene ring in III is to raise the pK_a of the cyclopentadiene moiety by *ca.* 11 units. This relative destabilization of III, by *ca.* 15 kcal/mol, probably contains some contribution from increased strain. However, it is also consistent with the hypothesis that the cyclobutadienoid resonance forms of III are appreciably antiaromatic.[8]

(8) Support of this work by the National Institutes of Health is gratefully acknowledged. These data were first reported at the National Organic Chemistry Symposium, Salt Lake City, Utah, 1969.

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Cuprous Complexes of Phenyldiazene

Sir:

Monosubstituted diazenes, which are exceedingly reactive and have defied isolation, have recently attracted considerable attention.[1] The work of Diels and Koll[2] has demonstrated the existence of complexes of the more stable 1,2-disubstituted diazenes with cuprous halides. These complexes, with the general constitution $(RN{=}NR)(CuX)_n$, may be formed either by treating a cuprous halide with the diazene or by the redox reaction between a cupric halide and a suitable hydrazine. An X-ray crystallographic study of a representative complex, $(CH_3N{=}NCH_3)Cu_2Cl_2$, has shown[3] that the compound consists of infinite chains of copper and chlorine atoms with the copper coordinated, roughly tetrahedrally, by three chlorine atoms in the chain and by a nitrogen lone pair from a diazene. The *trans*-diazene moiety bridges two cuprous chloride chains with the nitrogen atoms coordinated to copper atoms of two adjacent chains. In accord with their polymeric nature, compounds of this type have no true solubility in noncomplexing media. Since diazene complexes of this type may be prepared directly from a hydrazine without prior formation of the diazene and since the properties of these complexes are well established, we have endeavored to prepare similar complexes of the less stable monosubstituted diazenes.[4]

The addition of phenylhydrazine to an aqueous solution of cupric chloride produces a red-brown, somewhat air-sensitive complex, **1**, with the stoichiometry $(C_6H_5N{=}NH)Cu_4Cl_4$. A similar bromo complex is obtained analogously from cupric bromide. These complexes resemble other cuprous–diazene complexes. They exhibit no true solubility. Reaction of **1** with various Lewis bases results in the complete displacement of the diazene and the formation of Cu(I) complexes. For example, the reaction with dipyridyl produces $Cu(dipy)_2^+$ which can be isolated as the tetraphenylborate salt. In accord with its formulation as a cuprous complex, **1** is diamagnetic. The electronic spectrum obtained from a hydrocarbon mull of **1** shows a band at 455 nm; this is the region in which other cuprous–diazene complexes absorb.

The infrared spectrum of **1** is indicative of the presence of phenyldiazene. Only a single sharp band at 3130 cm^{-1} is observed in the region expected for the N–H stretching vibration. This vibration is shifted to 2320 cm^{-1} in the N-deuterated analog, which was prepared from $C_6H_5NDND_2$ in deuterium oxide. In contrast, authentic cuprous–phenylhydrazine complexes exhibit, as expected, several infrared bands in the N–H stretching region. For example, white $C_6H_5NHNH_2 \cdot CuI$, **2**, prepared by treating an aqueous potassium iodide solution of cuprous iodide with phenylhydrazine, has infrared absorptions at 3310, 3290, 3230, and 3150 cm^{-1}. It has not been possible to unambiguously assign a vibrational band to the N=N stretching frequency. Four bands at 1490, 1470, 1450, and 1420 cm^{-1} occur in the region where this vibration is expected.[5] Similar difficulties have been encountered in attempting to assign the N=N stretching vibration in 1,2-diphenyldiazene complexes.[5]

Pyrolysis of **1** produces detectable quantities of phenyldiazene in the vapor phase. The mass spectrum of the volatile species obtained from **1** using direct insertion techniques with a source temperature of 120° exhibits an intense peak at *m/e* 106.0531 (calcd for $C_6H_6N_2$, 106.0531). For the corresponding N-deuterated complex the most intense peak in this region occurs at *m/e* 107.6594 (calcd for $C_6H_5DN_2$, 107.6594). These peaks are not caused by fragmentation or pyrolysis of phenylhydrazine in either a complexed or free state. The relative intensities of the peaks at *m/e* 106 and 108 ($C_6H_5N_2H_3$) in the spectrum derived from **1** are in the ratio 35:1, whereas the mass spectrum obtained from the phenylhydrazine complex **2** under identical conditions exhibits peaks at *m/e* 106 and 108 in the ratio 1:15. Similarly in the mass spectrum of phenylhydrazine these peaks are in the ratio 1:17.

The complex **1** can be used as a convenient means of preparing acetonitrile solutions of phenyldiazene. It has been reported that phenyldiazene can be codistilled

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(1) (a) Phenyldiazene: P.-k. C. Huang and E. M. Kosower, *J. Amer. Chem. Soc.*, **90**, 2354, 2362, 2367 (1968); (b) substituted aryldiazenes: E. M. Kosower, P.-k. C. Huang, and T. Tsuji, *ibid.*, **91**, 2325 (1969); (c) methyldiazene: M. N. Ackermann, J. L. Ellenson, and D. H. Robison, *ibid.*, **90**, 7173 (1968); (d) *t*-butyldiazene: P.-k. C. Huang and E. M. Kosower, *ibid.*, **89**, 3911 (1967); (e) alkenyldiazenes: T. Tsuji and E. M. Kosower, *ibid.*, **91**, 3375 (1969).

(2) O. Diels and W. Koll, *Justus Liebigs Ann. Chem.*, **443**, 262 (1925).

(3) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, **13**, 28 (1960).

(4) Some examples of monosubstituted diazene complexes are known. The reaction of benzenediazonium ion with a platinum hydride complex produces a platinum complex of phenyldiazene: G. W. Parshall, *J. Amer. Chem. Soc.*, **89**, 1822 (1967); **87**, 2133 (1965). Complexes which may be considered as containing deprotonated diazenes have also been reported: R. B. King and M. B. Bisnette, *Inorg. Chem.*, **5**, 300 (1966); G. C. Dobinson, R. Mason, G. B. Robertson, R. Ugo, F. Conti, D. Morelli, S. Cenini, and F. Bonati, *Chem. Commun.*, 739 (1967). Spectroscopic and other evidence for the interaction of phenyldiazene and diazene (HN=NH) with ferroporphyrin and ferroheme proteins has been published: P.-k. C. Huang and E. M. Kosower *Biochim. Biophys. Acta*, **165**, 483 (1868): H. A. Itano and E. A. Robinson, *J. Amer. Chem. Soc.*, **83**, 3339 (1961); W. G. Hanstein, J. B. Lett, C. E. McKenna, and T. G. Traylor, *Proc. Nat. Acad. Sci. U. S.*, **58**, 1314 (1967).

(5) A. L. Balch and D. Petredis, *Inorg. Chem.*, **8**, 2247 (1969).

with acetonitrile; the electronic spectrum and chemical characteristics of such solutions have been recorded.[1a] Since acetonitrile forms a stable complex with Cu(I),[6] dissolution of **1** in acetonitrile should occur with the formation of $(CH_3CN)_4Cu^+$ and the liberation of the phenyldiazene. This, in fact, does occur. Dissolution of **1** in acetonitrile under the rigorous exclusion of molecular oxygen followed by careful distillation of the solution under the conditions described in ref 1a yields a solution of phenyldiazene as evidenced by its electronic spectrum (λ_{max} 417, 260, 215 nm) and by the rapid change in this spectrum upon exposure of the solution to molecular oxygen.

Stabilization of phenyldiazene in these complexes is probably due to simple physical isolation of the diazene, so that its reaction with other reagents, including itself, is inhibited. Attempts to prepare similar complexes of methyldiazene and benzyldiazene have been unsuccessful, although the reduction of Cu(II) to Cu(I) can be effected by both of the corresponding hydrazines. Steric factors may account for the failure to isolate complexes in these cases, since it is imperative that a suitable, stable lattice be formed to trap the diazene. A stable diazene complex has been formed from the reaction of cupric chloride with 1,1-dimethylhydrazine. This complex is characterized by a lack of any N–H stretching vibration in the infrared spectrum and the presence of an N=N stretching vibration at 1550 cm^{-1}. The infrared spectrum of this new complex is different from that of $(CH_3N{=}NCH_3)Cu_2Cl_2$, which does not exhibit an infrared-active N=N stretching frequency.[5] Treatment of the complex derived from 1,1-dimethylhydrazine with hydrochloric acid followed by neutralization yields tetramethyltetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$, in good yield. Although these results suggest that dimethyldiazene is not present in the complex; the coordinated species could be either 1,1-dimethyldiazene,[7] $(CH_3)_2N^+{=}N^-$, or its dimer, tetramethyltetrazene.[8] Experiments designed to differentiate between these two possibilities are in progress.

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[6] B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J. Chem. Soc.*, 3215 (1961).

[7] W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

[8] Isolation of tetramethyltetrazene from the complex after acidification and subsequent neutralization does not establish the presence of the tetrazene in the complex, since neutralization of acidic solutions thought to contain 1,1-dimethyldiazene is known to produce tetramethyltetrazene.[7]

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Vibrational Structure in the Electronic Absorption Spectrum of the Trapped Electron in Crystalline Acetonitrile-d_3 at 77°K[1]

Sir:

Solvated and trapped electrons are invariably characterized by a broad optical absorption in the visible or near-infrared. The nature of this electronic transition has been widely discussed for several different systems,[2] but progress has been hindered by the absence of any resolved structure in the band. In this communication, we report the discovery of vibrational fine structure in the optical absorption spectrum of a trapped electron in molecular crystals of acetonitrile-d_3. It is well known[3] that the electronic absorption spectra of molecules in crystals frequently show vibrational structure, especially at low temperatures.

We know from esr studies[4–8] that trapped electrons are produced in samples of crystalline acetonitrile-d_3 by γ irradiation at 77°K. The esr hyperfine structure of this paramagnetic species in quenched crystals is a quintet for the ^{14}N compound[4–6] and a triplet for the ^{15}N compound,[7] so it has been definitely established that the trapped electron interacts magnetically with two (and only two[8]) equivalent nitrogen nuclei. On photobleaching the sample with visible light at temperatures between 77 and 113°K, the esr spectrum of the trapped electron is replaced by the septet spectrum of $CD_3\cdot$. This change has been interpreted[4] as the *net* effect of dissociative electron capture. If the photobleached sample is kept in the dark, the reverse overall reaction occurs and the trapped electron is regenerated quantitatively at a rate which depends on the temperature. The activation energy for thermal recovery[8] is 4.6 kcal mole^{-1}.

The presence of a trapped electron in γ-irradiated acetonitrile-d_3 is indicated also by an optical absorption with λ_{max} at 510 nm. That the esr and optical absorption spectra refer to the same center has now been proved unequivocally by experiments showing that the optical spectrum is also restored thermally after photobleaching without any loss of intensity for the complete cycle.

Figure 1 shows the fine structure in the optical spectrum taken before photobleaching. The possibility that the undulations represent some artifact of the experimental optics is ruled out by the total disappearance of this structure in the spectrum recorded immediately after the sample had been photobleached *in situ* without change of cell position or other experimental conditions. Moreover, from a comparison of the spectra recorded in several different experiments using cells of different construction with two spectrophotometers, it is found that the positions of the peaks and troughs are exactly reproducible, and this fine structure is regained with perfect fidelity on thermal recovery after photobleaching.

Inspection of the entire spectrum reveals a long progression of more than 40 bands originating at 1.151×10^4 cm^{-1} with a mean separation of 306 cm^{-1}. This spacing is virtually constant within the precision of our measurements, although there appears to be a slight trend from 309 to 303 cm^{-1} over the entire absorption in the direction of increasing frequency, as deduced

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[2] For references, see J. Jortner and S. A. Rice, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 7.

[3] D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," Academic Press, New York, N. Y., 1959, p 24 ff.

[4] M. A. Bonin, K. Tsuji, and F. Williams, *Nature*, **218**, 946 (1968).

[5] M. A. Bonin, K. Takeda, and F. Williams, *J. Chem. Phys.*, **50**, 5423 (1969).

[6] K. Takeda and F. Williams, *Mol. Phys.*, **17**, 677 (1969).

[7] K. Takeda and F. Williams, unpublished work.

[8] M. A. Bonin, Ph.D. Thesis, The University of Tennessee, 1969.