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- (11) The program employed is a modification of the standard INDO (available from Q.C.P.E.) that can converge on different electronic configurations. Since the configurations under investigation are of different symmetry, this result can be easily achieved by changing in the appropriate way the occupation of the starting MO's and therefore the guess density matrix.
- (12) Laboratorio C.N.R. Ozzano Emilia, Bologna.
- (13) In partial fulfillment of the requirements for the doctoral degree of the University of Bologna.

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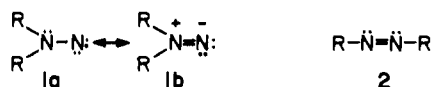
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Synthesis and Direct Spectroscopic Observation of a 1,1-Dialkyldiazene. Infrared and Electronic Spectrum of *N*-(2,2,6,6-Tetramethylpiperidyl)nitrene

Sir:

1,1-Dialkyldiazenes (aminonitrenes, *N*-nitrenes) **1**, unlike their more stable 1,2-dialkyldiazene isomers (azo compounds) **2**, have not yet been isolated or detected by spectroscopic



methods, but rather are assumed intermediates based on a substantial body of chemical evidence.¹ Chemical reactions of presumed 1,1-dialkyldiazene intermediates show behavior suggesting that the reacting species is a singlet¹ in contrast to other nitrenes, e.g., alkyl, aryl, carboxy, and cyano nitrenes ($R-N$), which are ground-state triplets.² The nature of the bonding and the relative energies of the states of the parent 1,1-diazene (H_2N-N) have been the subject of several theoretical investigations, which report that the singlet-triplet splitting may be quite small.³ Two recent calculations which include extensive configuration interaction predict the singlet is the ground state.^{3e,f} GVB-CI calculations by Goddard and Davis^{3f} indicate that the dipolar form **1b** makes a substantial contribution to the electronic structure of the 1,1-diazene (Figure 1). Of particular import to the experimentalist is the predicted $^1A_2 \leftarrow ^1A_1$ transition energy of 2.2 eV^{3f} which should be detectable by electronic absorption spectroscopy in the visible region (~ 558 nm).

We report here the synthesis and direct observation of a 1,1-dialkyldiazene, *N*-(2,2,6,6-tetramethylpiperidyl)nitrene (**3**). The visible spectrum provides the first experimental in-

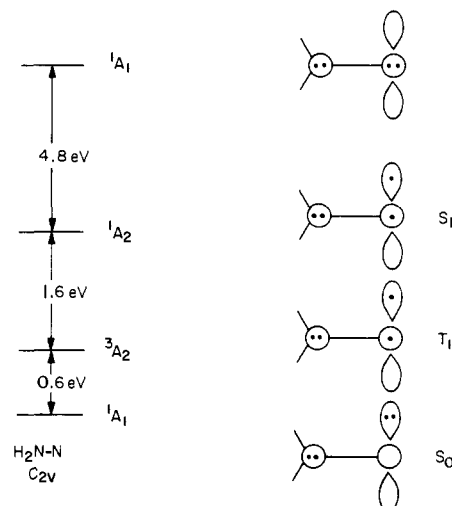
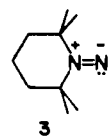


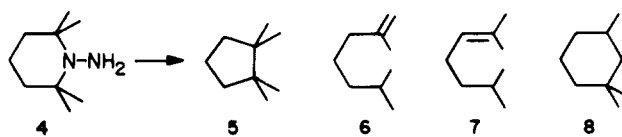
Figure 1. GVB-CI calculations^{3f} for H_2N-N (C_{2v} symmetry).

formation concerning the electronic structure of a 1,1-dialkyldiazene. Moreover, the infrared spectrum provides evidence that there is considerable double bond character in the $N=N$ bond, similar to a 1,2-diazene (**2**).



We were encouraged by work in the literature concerning the benefits derived from the synthesis of "persistent" carbon-centered radicals, radicals which may or may not be stabilized by resonance and inductive effects but which are long-lived and therefore subject to spectroscopic inspection because the rate of bimolecular reaction has been drastically slowed down by a steric blockade.⁴ It seems reasonable that ordinary elusive 1,1-diazenes with a suitable arrangement of bulky groups would become persistent and therefore easily prepared in relatively high concentrations which would allow their structural and chemical properties to be examined with an ease and accuracy impossible to attain with a transient species.

It is known that oxidation of 1-amino-2,2,6,6-tetramethylpiperidine (**4**) at 50 °C affords hydrocarbon products consistent with the formation and subsequent decomposition of a 1,1-dialkyldiazene intermediate.⁵ We find that addition of *tert*-butyl hypochlorite (*t*-BuOCl)⁶ to a stirred solution of **4** and triethylamine (Et_3N) in anhydrous diethyl ether at -78 °C affords, in addition to an insoluble white precipitate (Et_3NHCl), an intense purple solution which is stable for hours at -78 °C, but decolorizes in minutes at 0 °C. Hydrocarbon



products **5-8** are observed in 14-24% yield in a ratio of 9.7:2.5:24:1.0, respectively.⁷ Generation of this colored solution at -78 °C followed by filtration at -78 °C gives a clear purple solution. Low temperature absorption spectroscopy⁸ in the visible region on this solution at -78 °C reveals a structured absorption band with two *maxima* at 514 and 543 nm, remarkably close to the $n-\pi^*$ electronic transition¹⁰ predicted

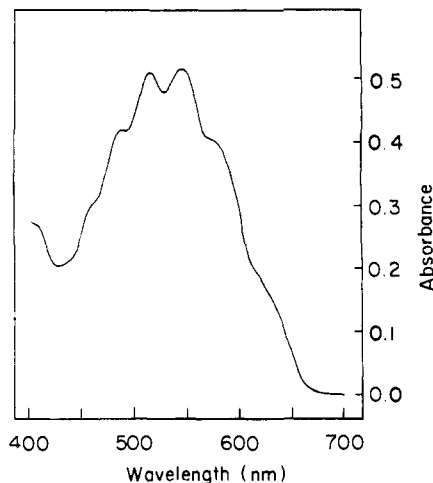


Figure 2. Visible spectrum of **3** at $-78\text{ }^{\circ}\text{C}$ in Et_2O .

by Goddard and Davis^{3f} for the parent system $\text{H}_2\text{N}-\text{N}^{\text{H}}$ (Figure 2).

The detail in this electronic spectrum appears to be vibrational structure. Although the spectrum is not sufficiently resolved to be able to read the wavelengths to any great accuracy, a crude analysis shows the spacings between maxima to be $\sim 1040\text{ cm}^{-1}$. Qualitatively, the overall appearance of the spectrum is in accord with that expected for a chromophore X-Y whose X-Y separation is slightly larger in the excited state than in the ground state.¹³ The energy difference between maxima in the electronic spectrum presumably corresponds to the vibrational level spacing in the excited state of the 1,1-diazene.

The position of an absorption that involves nonbonding electrons ($n \rightarrow \pi^*$) is particularly sensitive to the polarity of the solvent. The 1,1-dialkyldiazene chromophore is isoelectronic with ketones. We find the visible spectrum of the 1,1-diazene is subject to a blue shift with increase in solvent polarity analogous to solvent effects on the $n \rightarrow \pi^*$ transition of the carbonyl group.¹⁴ When *t*-BuOCl is added to **4** in the presence of Et_3N in dimethyl ether (Me_2O) at $-78\text{ }^{\circ}\text{C}$, filtered, concentrated, and diluted with dichloromethane (CH_2Cl_2), a λ_{max} at 541 nm is observed. However, if the Me_2O is replaced with isopropyl alcohol, a λ_{max} at 526 nm is observed, a shift of 15 nm to shorter wavelength (Figure 3). An interpretation consistent with the result is that the shift to higher energy for the $n \rightarrow \pi^*$ electronic transition in isopropyl alcohol results from stabilization of the ground state in the more polar solvent.¹⁵

When *t*-BuOCl is allowed to react with **4** in the presence of Et_3N , and the reaction mixture is filtered, concentrated, and diluted with CH_2Cl_2 at $-78\text{ }^{\circ}\text{C}$ and introduced into a copper-jacketed infrared cell (CsBr) at $-78\text{ }^{\circ}\text{C}$,⁹ the infrared spectrum shows a strong absorption at 1595 cm^{-1} that disappears on warming to $25\text{ }^{\circ}\text{C}$ (Figure 4a). This is suggestive of an $\text{N}=\text{N}$ double-bond stretching frequency.¹⁷ To test this, application of Hooke's law allows an approximation of the stretching frequency change for the appropriate $^{14}\text{N}=\text{N}$ isotopically labeled isomer.¹⁹ The calculated $\nu(^{14}\text{N}=\text{N})/\nu(^{14}\text{N}=\text{N})$ ratio is 1.0171 or a predicted shift to a lower wavenumber for the $^{14}\text{N}=\text{N}$ species to 1568 cm^{-1} . Synthesis of the corresponding $\text{R}_2^{14}\text{N}-^{15}\text{N}$ species (**10**)²⁰ affords an infrared spectrum with no absorption at 1595 but rather a new

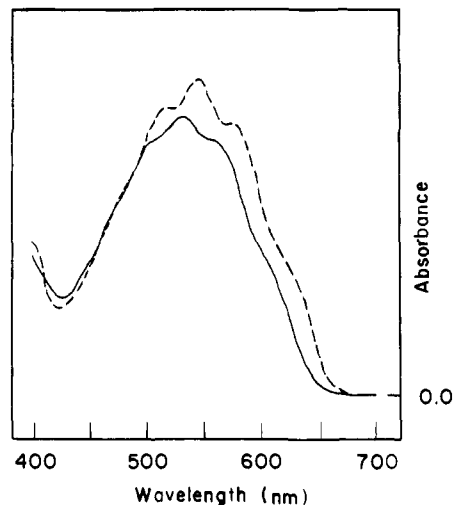
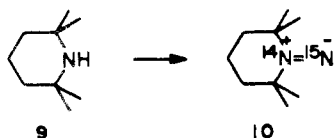


Figure 3. In CH_2Cl_2 , λ_{max} 541 nm (---); in *i*-PrOH, λ_{max} 526 nm (—).

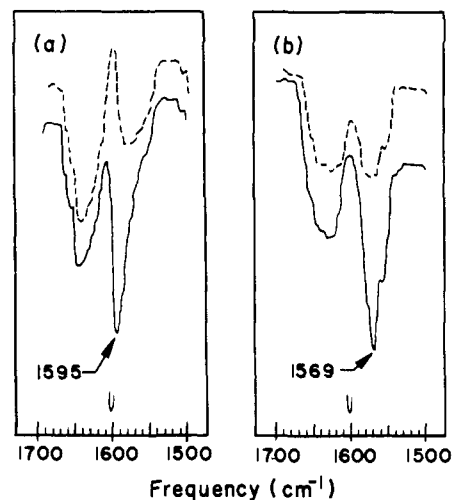


Figure 4. (a) $\text{R}_2^{14}\text{N}=\text{N}$; (b) $\text{R}_2^{14}\text{N}=\text{N}$. At $-78\text{ }^{\circ}\text{C}$ (—); at $-78\text{ }^{\circ}\text{C}$ after warming to $25\text{ }^{\circ}\text{C}$ (---).

absorption at 1569 cm^{-1} , a shift of 26 cm^{-1} consistent with the assignment to an $\text{N}=\text{N}$ stretch for the 1,1-diazene (Figure 4b). These results suggest that there is considerable double-bond character in the 1,1-dialkyldiazene $\text{N}=\text{N}$ bond, remarkably close to a 1,2-diazene isomer.¹⁷

In summary, the visible spectrum of the 1,1-dialkyldiazene provides experimental evidence on (1) the energy required for the $n \rightarrow \pi^*$ electronic transition, and (2) the vibrational spacing of the first electronically excited state. The infrared spectrum provides evidence that the 1,1-diazene has considerable $\text{N}=\text{N}$ double-bond character in the ground state. Finally, the ability to generate this species in reasonable concentration at $-78\text{ }^{\circ}\text{C}$ for hours gives us some idea of its thermal stability and should allow further investigations of the rate of thermal fragmentation, chemical reactivity, and photochemistry of 1,1-diazenes.

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- (8) The purple solution is introduced via Teflon tubing connected to sample injection ports into a specially designed copper-jacketed quartz cell attached to a cryogenic system⁹ maintained at -78 °C.
- (9) Air Products Laboratory cryogenic system, Model LC-1-100 liquid nitrogen Dewar assembly, Model WMX-1A optical shroud with injector ports.
- (10) A rough estimate of the extinction coefficient (ϵ) can be made based on the hydrocarbon yield. We calculate $\epsilon \sim 13$, for the $n \rightarrow \pi^*$ electronic transition of the 1,1-diazene.
- (11) Nils Wiberg and coworkers¹² recently reported the pyrolysis of lithium tosylhydrazide which deposited on surfaces cooled by liquid nitrogen a lustrous yellow solid diazene—*trans*-1,2-diazene (diimide)—which had λ_{\max} 386 nm. The pyrolysis of cesium tosylhydrazide deposits a different diazene which had λ_{\max} 260 nm. Wiberg was not able to assign this "other" diazene isomer to the *cis*-1,2-diazene or 1,1-diazene.
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- (15) Part of the blue shift could arise from the destabilization of the Franck-Condon excited state in the hydrogen bonding solvent.¹⁶
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- (17) The N=N stretching vibration of a symmetrical *trans* azo compound is forbidden in the infrared but absorbs in the 1576-cm⁻¹ (6.35 μ) region of the Raman spectrum.¹⁶
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- (20) Successive treatment of 2,2,6,6-tetramethylpiperidine (**9**) with Na¹⁵NO₂ (Prochemicals Limited, N. J.), lithium aluminum hydride,²¹ and *t*-BuOCl/Et₃N afforded the 1,1-dialkyldiazene **10**.
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- (22) National Science Foundation Predoctoral Fellow, 1975-1978.
- (23) Alfred P. Sloan Research Fellow, 1977-1979.

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A Structural Model for Type 3 Copper in Multicopper Oxidases

Sir:

In the multicopper (blue) oxidases type 3 copper exists in an EPR-nondetectable form and is associated with a two-electron accepting unit.¹ Magnetic susceptibility studies on oxidized *Rhus vernicifera* laccase (*p*-diphenol:O₂ oxidoreductase, E.C. 1.10.3.2) have established that the two type 3 copper atoms are present as an antiferromagnetically coupled Cu(II) dimer.² Although ligands bridging the coppers have not been positively identified, and other structural information is scanty, models incorporating two mercaptides or a disulfide as bridging ligands have received the most attention.^{1,3} In conjunction with our investigation of mercaptide-bridged intramolecular electron transfer,⁴ we have prepared and deter-

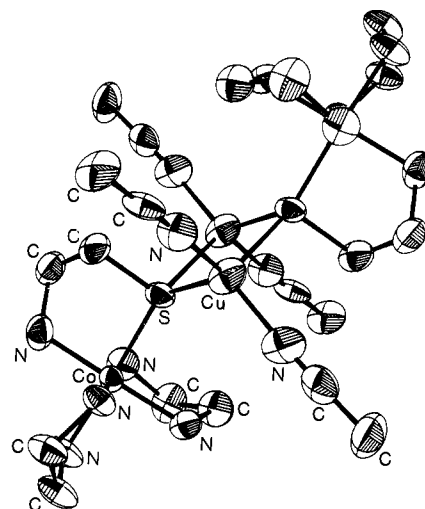


Figure 1. ORTEP drawing of the $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)\cdot\text{Cu}(\text{CH}_3\text{CN})_2]_2^{6+}$ cation. The 50% thermal probability ellipsoids are shown for all nonhydrogen atoms. Unlabeled atoms are related to the labeled ones by the crystallographic center of inversion.

mined by x-ray diffraction methods the crystal and molecular structure of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)\cdot\text{Cu}(\text{CH}_3\text{CN})_2]_2\cdot(\text{ClO}_4)_6\cdot 2\text{H}_2\text{O}$ (en = ethylenediamine) which contains a unique $\text{Cu}(\text{I})_2(\text{SR})_2$ planar unit. We believe this to be the first report of definitive structural information for such a copper-sulfur structure which is directly related to proposed models for the reduced form of type 3 copper in multicopper oxidases.

Addition of a concentrated solution of $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]_2^{2+}$ (perchlorate salt) in 0.1 M HClO_4 to excess solid $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$, followed by filtration, precipitation with solid sodium perchlorate, and recrystallization from dilute HClO_4 - NaClO_4 (all operations carried out under a nitrogen atmosphere), yields dull red-brown crystals which, when dry, are stable to air for several weeks. In anaerobic 0.1 M HClO_4 , a solution prepared from the crystals exhibits an absorption (λ_{\max} 365 nm (ϵ 2900)) indistinguishable from that observed for the 1:1 complex formed between $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]_2^{2+}$ and aqueous $\text{Cu}(\text{I})^4$ in which coordination of copper to sulfur is required by the fact that sulfur is the only potential ligand bridge between the two metals and is further supported by the disappearance of the sulfur-to-cobalt charge-transfer transition from 282 nm in the starting complex⁵ and the appearance of a new band at 365 nm upon incorporation of $\text{Cu}(\text{I})$.

The adduct formed rectangular crystals which were monoclinic, space group $P2_1/c$, with two molecules in a cell of dimensions $a = 10.070$ (3) Å, $b = 24.447$ (5) Å, $c = 11.497$ (3) Å, $\beta = 110.32$ (4)°. The calculated density was 1.795 g/cm³ for $Z = 2$, which compared well with the measured density of 1.74 (5) determined by flotation in ethylene bromide-chloroform. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using the ω - 2θ scan technique and $\text{Mo K}\alpha$ radiation. The structure was solved by direct methods using MULTAN; nonhydrogen atomic parameters were refined by full-matrix least-squares calculations using the 2246 independent observed reflections. The R value after anisotropic refinement of all nonhydrogen atoms was 0.096. Two of the three symmetry-distinct perchlorate groups were disordered and will be treated in the final refinement of the structure.

The structure consists of two cobalt(III)-mercaptide-copper(I) moieties linked by mercaptide bridges between the copper atoms as shown in Figure 1. The crystallographic inversion center is located within the resulting $\text{Cu}_2(\text{SR})_2$ planar