the identity of synthetic epiibogamine (19) with a sample prepared from catharanthine.[5] We have previously described a method for the introduction of a carbomethoxy group at C-18, which is present in the voacanga alkaloids.[6]

Acknowledgment. This work was supported by grants from the National Institutes of Health and from the Hoffmann-LaRoche Anniversary Foundation.

(5) M. Gorman, N. Neuss, and N. J. Cone, *J. Am. Chem. Soc.*, 87, 93 (1965). We are grateful to Dr. N. Neuss, Eli Lilly and Co., for sending us an authentic sample of epiibogamine.
(6) G. Büchi and R. E. Manning, *Pure Appl. Chem.*, 9, 21 (1964).
(7) Woodrow Wilson Fellow 1961–1962.
(8) National Institutes of Health Postdoctoral Fellow 1963–1964.
(9) National Science Foundation Postdoctoral Fellow 1964–1965.

G. Büchi, D. L. Coffen,[7] Karoly Kocsis
P. E. Sonnet,[8] Frederick E. Ziegler[9]

*Department of Chemistry, Massachusetts
Institute of Technology, Cambridge, Massachusetts*

Received March 29, 1965

The Electron Paramagnetic Resonance of Triplet CNN, NCN, and NCCCN

Sir:

We wish to report the observation, by electron paramagnetic resonance, of the ground-state triplets diazomethylene, $:C=N^+=N^-$ (I); cyanonitrene, $N\equiv C—\ddot{N}$ (II); and dicyanomethylene, $N\equiv C—\ddot{C}—C\equiv N$ (III). Of particular interest is the previously unknown CNN which is prepared from cyanogen azide, NCN_3 (IV), using ultraviolet light of wave length below 3000 Å. If CNN inserted into existing bonds, it could yield a diazomethane derivative directly. Unlike the aromatic methylenes and nitrenes in which one electron is largely localized at the divalent carbon or univalent nitrogen,[1] I–III have extensive delocalization of both unpaired electrons. As such, they are similar to monocyanomethylene which has been observed by Bernheim, *et al.*[2]

The precursors[3,4] were photolyzed with an Osram HBO-200 mercury lamp in fluorolube, perfluorodimethylhexane, or hexafluorobenzene matrices at 77 or 4°K. The spectra were obtained with a Varian V-4500 spectrometer with 100-kc. modulation. A single line in the region of 6500–8000 gauss was observed. The shape was characteristic of approximately linear molecules.[5] We were observing those molecules in the randomly oriented sample in which the external magnetic field was perpendicular to the molecular axis. The parameters characteristic of the triplet state were obtained[5] assuming $g = 2.0023$.

Photolysis of IV for 30 min. with $\lambda > 3000$ Å., gave NCN with $D_{II} = 1.544$ and $E_{II} < 0.002$ cm.$^{-1}$. Subsequent irradiation including $\lambda < 3000$ Å. for 3 min.

(1) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, 40, 2408 (1964), and references cited therein; G. Smolinsky, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, 35, 576 (1963).
(2) R. A. Bernheim, R. J. Kempf, P. W. Humer, and P. S. Skell, *J. Chem. Phys.*, 41, 1156 (1964). These workers have also observed derivatives of propargylene and diethynylmethylene which are iso-π-electronic with I–III: *ibid.*, to be published. We thank Dr. Bernheim for making their results available prior to publication.
(3) F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, 86, 4506 (1964).
(4) E. Ciganek, *ibid.*, 87, 652 (1965). Dr. Ciganek kindly supplied the hydrazone precursor for the diazomalononitrile.
(5) E. Wasserman, L. C. Synder, and W. A. Yager, *J. Chem. Phys.*, 41, 1763 (1964). A weak H_{z1} line was also visible with I.

gave CNN,[6] $D_I = 1.153$ and $E_I < 0.002$ cm.$^{-1}$, more intense than the NCN but with no observable diminution of the NCN. Thus the ground state of NCN does not seem to be a precursor of CNN. The production of the CNN by the above procedure appears to be more efficient than irradiation of a fresh sample of IV with unfiltered radiation for 3 min. Perhaps the >3000-Å. irradiation produces an intermediate, which could be a linear or cyclic isomer of IV, which readily photolyzes to CNN with $\lambda < 3000$ Å.

We would expect the light of lower energy to cause the least structural change, so that the assignment of NCN to the first triplet is reasonable. However, the main support comes from the close agreement of D_{II} with the equivalent spin–spin coupling, 2λ, obtained by Herzberg and Travis from the ultraviolet spectrum of II in the gas phase, 1.567 cm.$^{-1}$.[7] The <2% change is similar to the differences which have been observed with other triplets on varying the rigid matrix in e.s.r. experiments.[8] The close correspondence of the gas phase and rigid matrix results indicates that D is largely independent of environment, uniquely so for a quantity which is a measure of the distribution of the highest energy electrons in the molecule.

NCN may be viewed as composed of two $N=C—N\cdot$ radials occupying orthogonal orbitals on the same nuclei. Then the main contribution to D, which measures the magnetic dipole interaction of the unpaired electrons and is roughly proportional to $1/r^3$, is the interaction of the unpaired electrons on the same atom,[9] $\sum_i \rho_i^2 D_i$. Here ρ_i is the spin density in one orbital of the ith atom and D_i is $D_{NH} = 1.86$ cm.$^{-1}$ [10] if $i = $ N, and $D_{linearCH_2} = 0.74$ cm.$^{-1}$ [11] if $i = $ C. Assuming spin densities of $\rho_1 = \rho_3 = \rho_N = 0.62$, $\rho_2 = \rho_C = -0.24$, somewhat larger in absolute value than those of the allyl radical,[12] and including the two-center interactions[9] ($\sim +0.05$ cm.$^{-1}$), we find $D_{II} = 1.52$ cm.$^{-1}$. A negative spin density at the central atom is necessary to avoid a much lower computed value.

The assignment of the low wave length triplet to CNN is based on several factors. The formation occurs in dilute glassy samples so that it appears to be first order in IV. If photolysis removes a nitrogen molecule from IV, a CN_2 fragment remains. Since E measures the deviation from cylindrical symmetry, a zero value indicates that the species is linear and eliminates $N=N—\underline{C}$. With NCN not a possibility, CNN is the remaining choice. Assuming that the spin densities of the outer and inner atoms of CNN are the same as NCN, we have $D = 1.16$ cm.$^{-1}$. Although the close agreement with experiment must be partly fortuitous, it does give additional support for the assignment of CNN.

(6) Dr. D. E. Milligan has made parallel observations in the ultraviolet and infrared spectra resulting from the photolysis of IV in an argon matrix at 4°K. The structural assignments are the same as those given here: D. E. Milligan, private communication.
(7) G. Herzberg and D. N. Travis, *Can. J. Phys.*, 42, 1658 (1964).
(8) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. chim. phys.*, 61, 1663 (1964).
(9) E. Wasserman, *J. Chem. Phys.*, in press. The examples considered in detail in this reference are the systems discussed in ref. 2.
(10) R. N. Dixon, *Can. J. Phys.*, 37, 1171 (1959).
(11) Extrapolated value from CF_3CH, to be published; see also ref. 9.
(12) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 39, 2147 (1963).

In fluorolube suspension we observed $D_{\mathrm{III}} = 1.002$ and $E_{\mathrm{III}} < 0.002$ cm.$^{-1}$, compatible with a linear molecule. Assuming $\rho_1 = \rho_5 = 0.40$, $\rho_2 = \rho_4 = -0.20$, and $\rho_3 = 0.60$, values somewhat larger than the isoelectronic carbon radical,[12] we compute $D_{\mathrm{III}} = 0.97$ cm.$^{-1}$. One reason, among others,[9] for the larger effective spin densities in II and III is that the two π-radicals may not be independent. An exchange interaction may stabilize structures in which the two unpaired electrons are on the same atom and thus give rise to a larger D. Nitrogen, with its larger effective nuclear charge, would be particularly effective. Spin-orbit terms are also expected to give a positive contribution to the experimental values of D.[9]

In hexafluorobenzene, III gave two lines of characteristic shape[5] and $E = 0.0033$ cm.$^{-1}$. Since $E \neq 0$, the molecule is bent, presumably about the central carbon. By a procedure analogous to that used for the aromatic methylenes,[1,13] we conclude that the deviation from linearity is not more than 10–15°. Here the crystalline matrix may be able to induce slight changes in geometry.[14] With diphenylmethylene such changes were not observed.[8]

Acknowledgments. We wish to thank Mr. R. M. R. Cramer for his aid in determining the spectra. We are also indebted to Drs. E. Ciganek, F. D. Marsh, D. E. Milligan, and H. E. Simmons[15] for helpful discussions.

(13) J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963).

(14) An alternative explanation of the apparent $E \neq 0$ is a distribution of values of D_{III}, due to different sites in the solvent, but with III still linear.

(15) Drs. A. G. Anastassiou and H. E. Simmons, of the Central Research Department, E. I. du Pont de Nemours and Co., are attempting to observe chemical reactions of I.

E. Wasserman, L. Barash, W. A. Yager

Bell Telephone Laboratories, Inc.
Murray Hill, New Jersey

Zinc(II) and Cobalt(II) Phosphinate Polymers with Low-Temperature Flexibility

Sir:

In developing the scope of tetrahedral metal phosphinate polymers,[1] we have introduced a variety of groups on the phosphorus. Preliminary results recently reported on the characterization of cobalt(II) and zinc(II) dibutylphosphinates[2] prompt us to present at this time some of our key observations on the polymers containing long alkyl side chains. Both of the noteworthy attributes that distinguish these materials from other cobalt(II) and zinc(II) phosphinates, namely, their surprisingly good low-temperature properties and their high intrinsic viscosities in a "good" solvent, were not described.

While many of the phosphinates we have reported in the past[1] are tractable, those that can be fabricated are brittle, glass-like solids at room temperature. We find, however, that zinc(II) and cobalt(II) phosphinate polymers containing long alkyl side chains appear to have very low glass transition temperatures. These are the first double-bridged polymers prepared with good low-temperature properties.

In order to stabilize the amorphous form of these polymers, it is necessary to introduce disorder into their structures. We have accomplished this by making polymers containing two kinds of bridging groups—a class of copolymers which we have termed *hybrid polymers*.[1b] The low-temperature properties of some of these double-bridged materials compare favorably with those of the better single-bridged polymers. For example, the nitroso rubbers,[3] which are promising potential low-temperature elastomers, become brittle at about $-50°$. In comparison, films of the hybrid polymer of zinc(II) with $OP(C_4H_9)_2O^-$ and $OP(C_8H_{17})_2O^-$ bridging groups in 1:1 ratio are flexible to below $-80°$.

The general procedure we have used to prepare these polymers is to reflux a mixture of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ or $Co(C_2H_3O_2)_2 \cdot 4H_2O$ with a solution of the stoichiometric amount of the appropriate phosphinic acid or acids in ethanol and recover the polymer by filtration.

Zinc(II) dibutylphosphinate has a molecular weight greater than 10,000 by vapor pressure osmometry in chloroform and intrinsic viscosities in chloroform ranging from 0.35 to 0.7 dl./g. The waxy solid isolated, which gives a crystalline X-ray powder pattern, may be converted into a metastable amorphous form by melting it ($\sim$250°) and then rapidly cooling it to below room temperature. This amorphous form turns brittle at approximately $-40°$. On standing at room temperature it gradually turns crystalline.

Anal. Calcd. for $C_{16}H_{36}O_4P_2Zn$: C, 45.8; H, 8.6; P, 14.8; Zn, 15.6. Found: C, 45.8; H, 8.7; P, 14.9; Zn, 15.3.

Zinc(II) dioctylphosphinate is similar. Its molecular weight also exceeds 10,000 by vapor pressure osmometry in chloroform, and its intrinsic viscosity is approximately 0.6 dl./g. The waxy solid, found to be crystalline in polarized light, does not completely melt before decomposing and hence is difficult to convert to the amorphous form.

Anal. Calcd. for $C_{32}H_{68}O_4P_2Zn$: C, 59.7; H, 10.6; P, 9.6; Zn, 10.2. Found: C, 59.7; H, 10.9; P, 9.6; Zn, 10.1.

Typical samples of the hybrid polymer of zinc(II) with $OP(C_4H_9)_2O^-$ and $OP(C_8H_{17})_2O^-$ bridging groups in 1:1 ratio have molecular weights greater than 10,000 in chloroform by vapor pressure osmometry and intrinsic viscosities in chloroform on the order of 0.4 to 0.5 dl./g. The waxy powder, also crystalline in polarized light, melts at approximately 150° to an amorphous form which appears to remain amorphous indefinitely. It can be fabricated into films and other shaped articles at 200° under slight pressure. The molded objects are transparent, very flexible, and exhibit good leathery recovery. They hold their shape at 100° and remain fairly flexible when immersed in Dry Ice.

Anal. Calcd. for $C_{24}H_{52}O_4P_2Zn$: C, 54.2; H, 9.9; P, 11.6; Zn, 12.3. Found: C, 54.7; H, 10.1; P, 11.6; Zn, 11.9.

The corresponding cobalt(II) polymers are, in general, similar to their zinc(II) counterparts; they have sizable molecular weights by vapor pressure osmometry in chloroform and intrinsic viscosities in chloroform of

(1) (a) B. P. Block, S. H. Rose, C. W. Schaumann, E. S. Roth, and J. Simkin, *J. Am. Chem. Soc.*, **84**, 3200 (1962); (b) S. H. Rose and B. P. Block, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 11-O.

(2) V. Crescenzi, V. Giancotti, and A. Ripamonti, *J. Am. Chem. Soc.*, **87**, 391 (1965).

(3) J. C. Montermoso, *Rubber Chem. Technol.*, **34**, 1521 (1961).