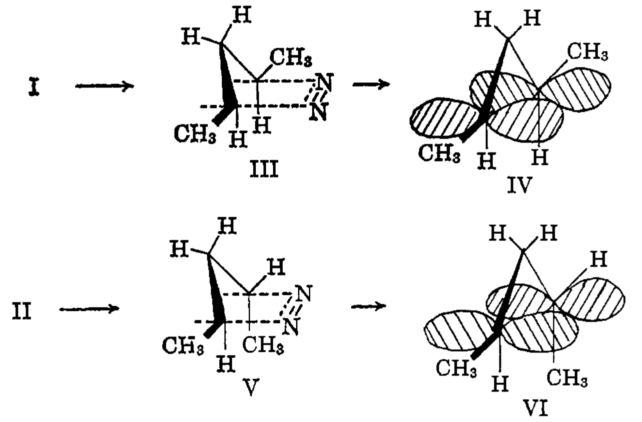
dominantly to *trans*-1,2-dimethylcyclopropane requires the diradical intermediate to undergo conrotation.[6] Similarly conrotation of VI results in II being transformed into *cis*-1,2-dimethylcyclopropane.[7]



The olefins may be explained by migration of either of the methylene hydrogens in IV to the radical centers giving only *trans*-2-pentene. When either of the methylene hydrogens in VI migrates to C-3 then *trans*-2-pentene is produced, but migration of a hydrogen atom to C-5 results in the formation of *cis*-2-pentene.[8]

That the transition state resembles III and IV is supported by the kinetic data in Table II. The 4,4-dimethyl-1-pyrazoline reacts at less than one-one-hundredth the rate of 1-pyrazoline even though one methyl group introduced into the 4-position has no effect upon the rate. The second methyl group places a methyl on C-4 on the same side as the departing nitrogen in the transition state; thus the reaction rate is decreased by making the desired transition state conformation less accessible.

Table II. Kinetics of Pyrazoline Decomposition

1-Pyrazoline	Temp., °C.	10^4k, sec.$^{-1}$	Rel. rate
I	197.0	5.42	
II	197.0	8.06	
Unsubstituted	223.0	16.0	1.00
4-Methyl-	223.0	15.5	0.97
4,4-Dimethyl-	223.0	0.126[a]	0.0079

[a] Extrapolated from rates in the range 250–285°.

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they are "π-cyclopropanes" wherein they gain some stability by π-bond formation between C-3 and C-5 is not experimentally distinguishable; however, both can serve the purpose of the intermediate. The "π-cyclopropane" would be equivalent to a "hot cyclopropane" with the excess energy localized between C-3 and C-5. If a normal tetrahedral angle is assumed for C-4 then the C-3 to C-5 distance 2.48 Å. results in a Slater overlap integral for $p_\pi p_\pi$ bonds of 0.025, less than one-tenth that of ethylene (see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons Inc., New York, N. Y., 1961, p. 16). Thus the energy gained from overlap approximates that of the repulsion for the two opposed hydrogens. We have thus chosen to refer to the species as a diradical.

(6) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965); H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965). Applying the method of Longuet-Higgins and Abrahamson one finds the π^2-configuration of the intermediates (IV and VI) correlate with the σ^2-configuration of the dimethylcyclopropanes no matter whether con- or disrotation is involved.

(7) M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), **A257**, 122 (1960), have shown *trans*-1,2-dimethylcyclopropane to be thermodynamically more stable than the *cis* isomer: ΔH = 1.07 kcal./mole at 380°.

(8) Stereospecific olefin formation in pyrazoline decompositions have recently been observed by D. E. McGreer, *et al.*, *Can. J. Chem.*, **43**, 1407 (1965). They advance a somewhat analogous explanation involving a concerted migration of the hydrogen *trans* to the departing nitrogen.

(9) National Research Council of Canada Scholarship holder, 1964–1965.

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Helium Difluoride

Sir:

We have constructed a many-electron valence bond wave function for HeF_2 and find a repulsive molecular energy curve for all geometries explored. The calculation was carried out using all twenty electrons, the exact, nonrelativistic Hamiltonian within the Born–Oppenheimer approximation, and all terms in the energy expression were consistently evaluated to high precision (eight significant figures). This is the first attempt to make a rigorous and unambiguous theoretical prediction of the properties of noble gas molecules and also represents one of the largest molecules yet treated in such a complete manner. All previous quantum mechanical experience indicates that our wave function is expected to be of high accuracy for this system.

The chemical structures included were[1] F He F, F^- He^+ F + F He^+ F^-, F^- He F^+ + F^+ He F^-, and F^- He^{2+} F^-.

In general, each of these structures corresponds to many states differing in orbital occupancy, and the states in turn are composed of sums of 20-row determinantal functions with symmetry-determined coefficients. Symmetric arrangements of atoms on a line lead to 11 states and 33 determinants, asymmetric linear arrays to 18 states and 33 determinants, and off-line equal bond length arrangements to 18 states with 53 determinants. These states represent a complete configuration interaction calculation with a ground-state atomic orbital basis (except for the chemically insignificant excitations of the fluorine 1s electrons). Our molecular wave function is formulated with nonorthogonal atomic orbitals and the energy is expressed in terms of Löwdin's overlap determinants.[2] The atomic orbitals are close to Hartree–Fock solutions and all one- and two-electron, one-, two-, and three-center integrals over these orbitals were evaluated consistently *via* a Gaussian-expansion technique[3] to nine significant figures. Molecular potential energy curves were obtained for three geometrical types: linear symmetric, linear asymmetric, and bent configurations with the He atom midway between the fluorine atoms. Representa-

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(1) Structures for He^- are omitted because helium cannot accept an electron.

(2) P. O. Löwdin, *Phys. Rev.*, **97**, 1474, 1490 (1955).

(3) J. L. Whitten, *J. Chem. Phys.*, **39**, 349 (1963); J. L. Whitten and L. C. Allen, *ibid.*, in press.

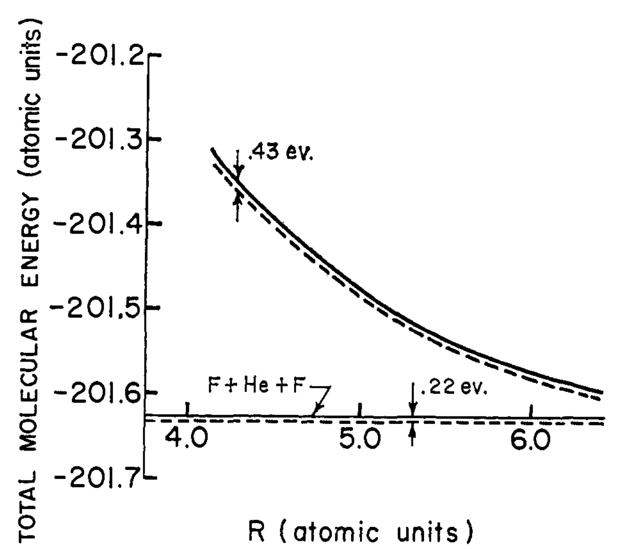

Figure 1. Energy of HeF_2 relative to F + He + F for linear symmetric geometry.

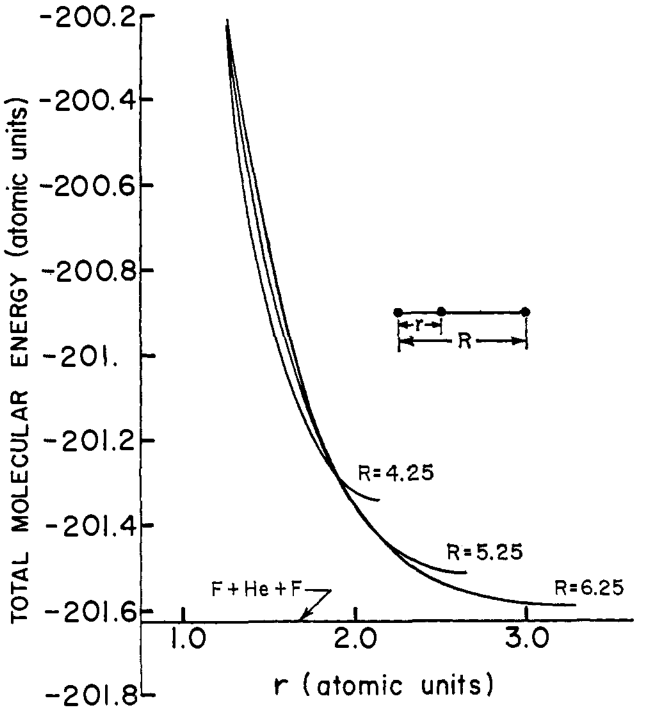

Figure 2. Energy of HeF_2 relative to F + He + F for linear asymmetric geometry.

tive curves are shown in Figures 1–3, and total energies for the symmetric stretch are given in Table I. The chemically most significant states with their approximate weights for the linear symmetric wave function at a separation near to that expected if the molecule were stable (F–F distance = 4.25 a.u. = 2.25 Å.) are given by

$$\begin{aligned}\Psi \cong\ & +0.621\{F(1s)^2(2s)^2(2p_\sigma)(2p_\pi)^4 \times \\ & \qquad He(1s)^2F(1s)^2(2s)^2(2p_\sigma)(2p_\pi)^4\} \\ & +0.432\{F(1s)^2(2s)^2(2p_\sigma)(2p_\pi)^4He(1s) \times \\ & \qquad F(1s)^2(2s)^2(2p)^6\} \\ & +0.150\{F(1s)^2(2s)^2(2p_\pi)^4He(1s)^2F(1s)^2(2s)^2(2p)^6\} \\ & +0.70\{F(1s)^2(2s)(2p)^6He(1s)^2F(1s)^2 \times \\ & \qquad (2s)^2(2p_\sigma)(2p_\pi)^4\}\end{aligned}$$

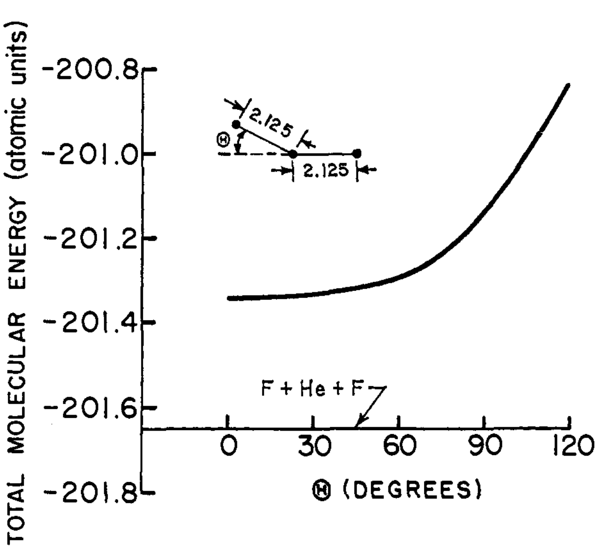

Figure 3. Energy of HeF_2 relative to F + He + F for bending mode (equal F-He separations).

The sizable ionic contribution represented by the two middle terms with structures F He^+ F^- and F^+ He F^-, respectively, shows the same ionic tendency present in the stable molecule XeF_2.

Table I. Energies for Linear Symmetric HeF_2

R[a]	Total molecular electric energy[b]	Nuclear repulsion, a.u.	Resultant energy,[c] e.v.
4.25	−237.34364	+36.00000	+7.66
5.25	−230.65631	+29.14285	+3.05
6.25	−266.06666	+24.48000	+1.06

[a] F–F separation in a.u. = 0.529 Å. [b] Atomic units = 27.206 e.v. [c] Above free atoms. Total atomic energy = 2F + He = 2(−99.382324) + (−2.8608632) = −201.62551 a.u.

In addition to the ionic states discussed above we have also carried out calculations including further configuration interaction:

(1) In-out or split orbital, (1s)(1s′), flexibility has been introduced into the He orbital. Results for a nonoptimized version of this are shown by the dotted line on the linear symmetric curve (Figure 1). The total atomic energy is lowered 0.22 e.v. and the total molecular energy 0.43 e.v. by this process.[4]

(2) A He $2p_\sigma$ function has been introduced. For linear HeF_2 at $R = 4.25$, $r = R/2$, this lowers the total molecular energy by a very small value, 0.125 e.v.

Probably the strongest reason for belief in the HeF_2 repulsive potential energy surface reported here is the existence of a complete potential surface for $[FHF]^-$ that we have obtained by the identical many-electron valence bond method. The $[FHF]^-$ potential surface shows a single minimum at 4.25 a.u. and other features very close to those known experimentally.[5]

Without any reference at all to the elaborate calculation we have described, everyone knows that the

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(4) Additional details of our calculations including results for asymmetric bent geometries are to be submitted for publication.

(5) R. M. Erdahl and L. C. Allen, to be submitted for publication.

simplest chemical rule regarding ionization potentials (He first I.P. = 24.58 e.v.; F first I.P. = 17.42 e.v.) leads to the conclusion that HeF_2 is highly unlikely to be bound. This prediction based on this qualitative argument has been stated several times in recent theoretical treatments,[6-8] yet, not unexpectedly, this simple argument is stated with considerably less conviction than would be expressed by a chemist who had no knowledge of xenon chemistry. In fact, a detailed and well-reasoned communication has been published claiming the likely existence of a stable HeF_2.[9] It is for these reasons that the qualitative chemical arguments and their manifestation in terms of simple Hückel-like model theories[6-8,10] are subject to the "strong inference" criticism of Platt[11] and are inadequate to answer decisively the question of the existence of HeF_2. It is also necessary that the electronic wave function for the HeF_2 system be complete enough to provide a description of the free helium atom at the same level of accuracy as that needed to produce a smooth change from a free xenon atom at infinite separation to the observed stable binding. This has been accomplished in our wave function by carrying the ionic state and in-out configuration interaction into the free helium atom as infinite separation is approached.

(6) R. M. Noyes, *J. Am. Chem. Soc.*, **85**, 2202 (1963).

(7) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

(8) C. A. Coulson, *J. Chem. Soc.*, 1442 (1964).

(9) G. C. Pimentel and R. D. Spratley, *J. Am. Chem. Soc.*, **85**, 826 (1963). Also see G. C. Pimentel, R. D. Spratley, and A. R. Miller, *Science*, **143**, 674 (1964).

(10) J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 825 (1963).

(11) J. R. Platt, *Science*, **146**, 347 (1964).

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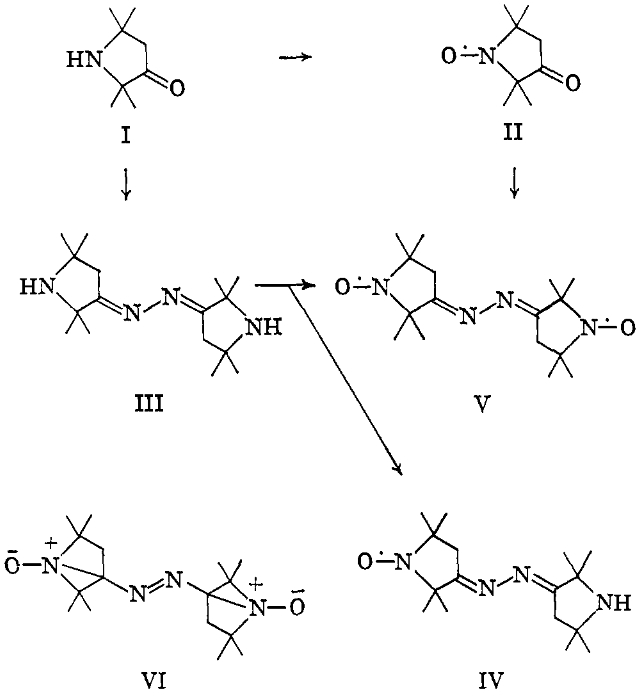
Nitroxides. XIV. A Stable Biradical in the Nitroxide Series

Sir:

We wish to report the synthesis of a stable biradical of the nitroxide series which exhibits a particularly evident coupling between the two unpaired spins.

Condensation of 2,2,5,5-tetramethyl-3-pyrrolidone[1] (I) with hydrazine in refluxing diethylene glycol gave the azine III, m.p. 157°. Oxidation of this azine with hydrogen peroxide in the presence of phosphotungstic acid[2,3] gave a mixture, separated by chromatography on alumina, of the monoradical[4] IV, m.p. 147° (from petroleum ether; 29% yield), and the biradical[4] V, mol. wt. 308 (mass spectrometry), large yellow crystals, m.p. 198° (from benzene, 18% yield).

The biradical V can also be obtained from IV by the same oxidation process (23% yield) or by treating a crude solution[5] of II[6] with hydrazine in diethylene glycol (14% yield).



The ultraviolet [λ_{max} 427.5 mμ (ϵ 17.7), to be compared with the known values (ϵ <10) of analogous nitroxides[4,5,7] and to IV, λ_{max} 427.5 mμ (ϵ 8.9)] and infrared spectra (no absorption in the N-H region, C=N band at 1660 cm.$^{-1}$) confirm the structure: V is composed of two independent nitroxide moieties similar to II. This excludes any structure related to VI. Furthermore, the intensity of e.p.r. absorption of a polycrystalline sample of V is 2.16 times the absorption of a polycrystalline sample of IV containing the same number of molecules.

However, the e.p.r. spectrum of V in solution is very different from spectra of cognate nitroxides[5,6]: while the monoradical IV displays the classical triplet (intensity ratio 1:1:1, a_N = 14.40 oersteds in dimethylformamide, g = 2.0055) corresponding to the hyperfine interaction of the unpaired electron with one nitrogen nucleus (Figure 1a), the biradical V shows a well-resolved quintet (Figure 1b) associated with the interaction of each unpaired electron with the nitrogen nuclei of the two equivalent nitroxide groups (intensity ratio 1:2:3:2:1, a_N = 7.20 oersteds in dimethylformamide, g = 2.0055). Thus, the important conclusion drawn from the e.p.r. spectrum is that this biradical behaves like a triplet state where the unpaired electrons present an exchange interaction greater than the hyperfine interaction.[8-10] However, coupling of electrons is neither sufficient to displace the absorption of the $n \rightarrow \pi^*$ transition in the ultraviolet spectrum nor sufficient to broaden the lines of the e.p.r. spectrum by dipolar interaction.[11] So, in the study of electronic interactions in organic molecules, the biradical V takes place between Chichibabin biradical,[9] where the hyperfine structure characterizes the inde-

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(4) Satisfactory microanalysis has been obtained for this new compound.

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