

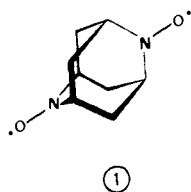
Nitroxides. LII. Synthesis and Electron Spin Resonance Studies of N,N' -Dioxy-2,6-diazaadamantane, a Symmetrical Ground State Triplet

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Abstract: Starting from norpseudopelletierine, syntheses of two monoradical nitroxides and of a biradical nitroxide with a diazaadamantane skeleton are described. ESR and nmr measurements on monoradicals are reported and interpreted. In the solid state, the pure N,N' -dioxy-2,6-diazaadamantane biradical is diamagnetic. Its ESR spectrum in glassy solution is typical of an axially symmetric triplet: $D = 250$ G. It shows resolved hyperfine structures from both nitrogen nuclei. Isotropic and anisotropic hfsc's have been determined: $a_N = 20$ G, $A_N^{zz} = A_N^{yy} = 13$ G, $A_N^{xx} = 34$ G. Although poorly resolved due to the large dipolar interaction, a hyperfine structure is observed in dilute solution. Singlet-triplet splitting is measured: $|J| = 170^\circ\text{K} = 0.3$ kcal/mol = 110 cm $^{-1}$ = 3×10^6 MHz. The biradical is found to be a *ground state triplet*. This may be attributed to its D_{2d} symmetry.

It is well known that stable nitroxide biradicals¹ afford a great variety of two-electron interacting systems and therefore provide good examples for testing theoretical work.² Examples in which the electron-electron dipolar interaction is large have been reported,³ but none has been designed specifically to present a zero field dipolar tensor with axial symmetry. We have synthesized such a bisnitroxide radical with an adamantane structure, N,N' -dioxy-2,6-diazaadamantane, **1**,^{3b} and we report its chemical and spectroscopic properties.



(I) Preparation of Monoradicals and Biradical Derived from Pseudopelletierine

The adamantane skeleton was constructed from pseudopelletierine, **2**, in two steps (Scheme I).⁴ Step a shows the introduction of a second nitrogen atom on 9-azabicyclo[3.3.1]nonan-3-one. This reaction is a standard reductive amination and gives 3- α -benzylaminopseudopelletierine, **3a** ($R_1 = \text{H}$, $R_2 = \text{CH}_2\text{-C}_6\text{H}_5$).⁵

Step b shows a ring closure to create the symmetrical diazaadamantane ring system. The favor-

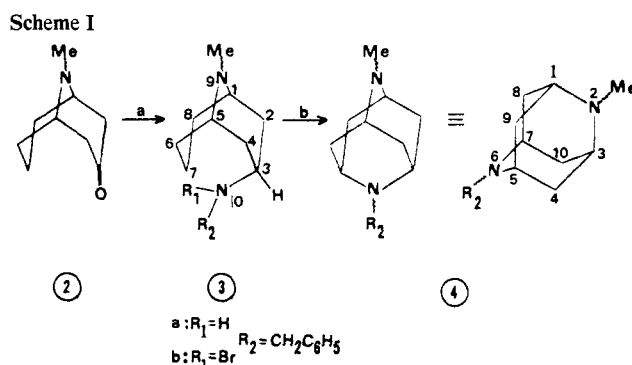
(1) (a) R. M. Dupeyre, H. Lemaire, and A. Rassat, *J. Amer. Chem. Soc.*, **87**, 3771 (1965); (b) E. G. Rozantsev, V. A. Golubev, M. B. Neiman, and Yu. V. Kokhanov, *Bull. Acad. Sci. USSR*, 559 (1965); (c) R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

(2) (a) H. Lemaire, Thesis, Grenoble, 1966; Rapport CEA No. R 3119; (b) H. Lemaire, *J. Chim. Phys.*, **64**, 559 (1967).

(3) (a) A. Calder, A. R. Forrester, P. G. James, and G. R. Luckhurst, *J. Amer. Chem. Soc.*, **91**, 3724 (1969); (b) A. Rassat, *Pure Appl. Chem.*, **25**, 623 (1971); (c) J. F. W. Keana, R. J. W. Keana, and R. J. Dinerstein, *J. Amer. Chem. Soc.*, **93**, 2810 (1971); (d) A. Rassat and H. U. Sieveking, *Angew. Chem.*, **84**, 353 (1972); (e) J. Michon and A. Rassat, French Patent EN 7115999, May 4, 1971.

(4) (a) R. M. Dupeyre and A. Rassat, French Patent EN 7033438, September 1970; (b) *Tetrahedron Lett.*, **29**, 2699 (1973).

(5) S. Archer, T. R. Lewis, and M. J. Unser, *J. Amer. Chem. Soc.*, **79**, 4194 (1957).



able relative spatial position of the C_7 and N_{10} atoms leads us to choose the Hoffmann-Löffler reaction, even though this reaction is known to be a selective general synthesis of pyrrolidines. To our knowledge, only two cases have been reported in which a piperidine ring is formed.⁶

N -Bromobenzylamine, **3b** ($R_1 = \text{Br}$, $R_2 = \text{CH}_2\text{-C}_6\text{H}_5$), was obtained from N -benzylamine, **3a**, and bromine in cyclohexane. This compound was reacted with 85% sulfuric acid at 65° , followed by treatment with alkali, to give 2-methyl-6-benzyl-2,6-diazaadamantane, **4**. Total yield for the cyclization was 25% from the N -benzylamine, **3a**. Structure **4** is in agreement with both spectral and analytical data. The nuclear magnetic resonance (nmr) spectrum was particularly interesting in that besides N -methyl singlet and N -benzyl peaks, there were only two broad peaks at $\delta = 2.9$ and 1.9 ppm (in dideuteriomethylene chloride), with intensity ratio 4:8. This is typical of a very symmetrical molecule.

Monoradicals N -oxy-2,6-diazaadamantane, **5**, N -oxy-2-methyl-2,6-diazaadamantane, **7**, and biradical **1** were prepared as shown in Scheme II.

N -Debenzylation of 2-methyl-6-benzyl-2,6-diazaadamantane, **4**, gave 2-methyl-2,6-diazaadamantane, **6** (as proved by the disappearance of the $\text{CH}_2\text{-C}_6\text{H}_5$ peaks in the nmr spectrum of **4**), which, by oxidation with hydrogen peroxide in the presence of phospho-

(6) H. E. Wolff, *Chem. Rev.*, **63**, 55 (1963).

At 100 MHz the nmr spectrum of a solution of monoradical **5** in liquid nitroxide *N*-oxy-2,2,5,5-tetramethyloxazolidine and deuteriomethylene chloride (Figure 1b) shows three broad peaks in addition to the oxazolidin-oxyl¹⁵ lines: relative to TMS, peaks A and B in lower fields and peak C in higher fields. Another peak D is observed, whose intensity changes with time. It is attributed to some paramagnetic decomposition product. The paramagnetic shifts give the hfsc's: $a_H = +2.05$ G, $a_H = +1.3$ G, $a_H = -0.7$ G. The areas of these three peaks are respectively 2:6:4 (peaks A, B, C). These data are consistent with the C_{2v} symmetry of 2,6-diazaadamantane structure if we assume the nitroxide group to be planar or bent with fast inversion.

We are not able to distinguish experimentally between these two possibilities. A similar problem has already been studied¹⁶ and we favor a bent nitroxide group in fast inversion. By analogy with tropinone nitroxide¹¹ it is reasonable to attribute the largest splitting (+2.05 G) to bridgehead protons attached to C₃ and C₇ carbon atoms, and the four negative (-0.7 G) and four positive (+1.3 G) hfsc's to protons attached to C₁, C₈, C₉, and C₁₀ carbon atoms. The difference in magnitude between esr and nmr data may be ascribed¹⁷ to a reversible monomer-dimer equilibrium.¹⁸ The axial protons have a negative hfsc and the equatorial protons a positive hfsc.¹⁹ Consequently, the two other protons attached to C₁ and C₃ are attributed to the positive hfsc of +1.3 G.

Monoradical **7** displays the same esr features. It can be distinguished from monoradical **5** by its infrared (ir) spectrum. These two monoradicals are stable for only a few hours, in contrast to norpseudopelletierine nitroxide^{10a} and biradical **1**.

(2) **Biradical 1**. Like monoradicals **5** and **7**, biradical **1** is diamagnetic in the solid state (yellow needles).

The esr spectrum of a freshly prepared dilute solution (0.002 M) of biradical **1** in dimethylformamide (DMF) shows a three-line spectrum (Figure 2a): $a_N = 18.2$ G and $g = 2.0061$. When this freshly prepared solution is slowly heated, the three lines broaden. At 100°, a broad line (peak to peak line width = 40 G and $g = 2.0062$) is observed showing a poorly resolved hyperfine structure (Figure 2b). By cooling, the three-line spectrum is again observed without change in intensity. We have verified that some nitroxide monoradical mixed with biradical **1** always shows three narrow lines; for instance in DMF, 1,5,7-trimethylnorpseudopelletierine nitroxide monoradical²⁰ (0.0001 M) mixed with the biradical (0.002 M) gave $a_N = 17$ G and $\Delta H \approx 3$ G. Thus, even in very dilute solution, any trace of mono-

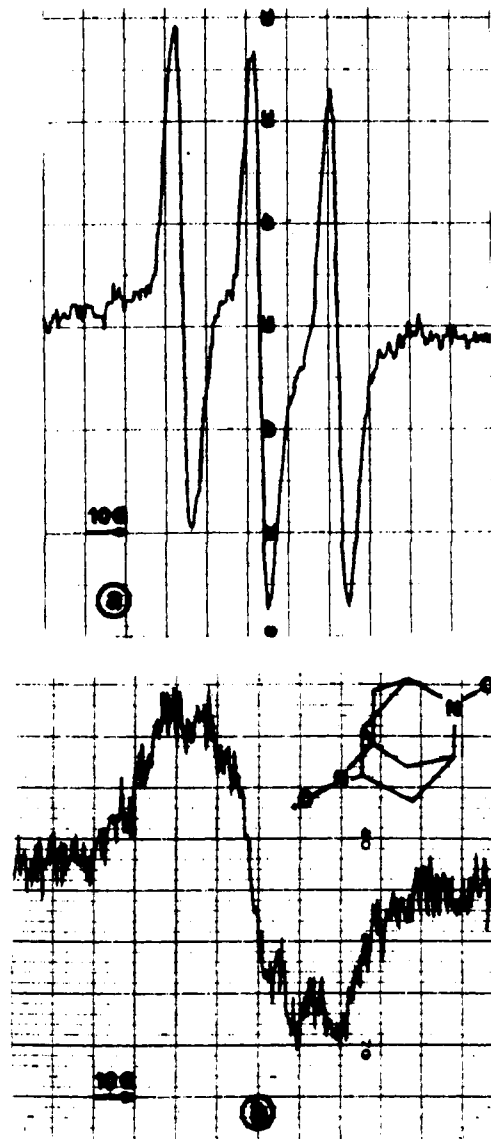
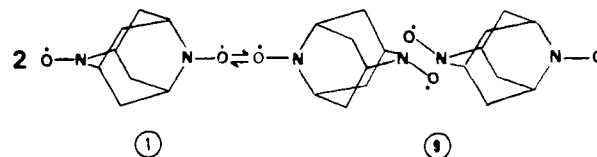


Figure 2. (a) ESR spectrum of a solution (0.002 M) of biradical **1** in DMF at room temperature. (b) ESR spectrum of this solution at 100°.

radical can be detected. The ir spectrum of biradical **1** does not show absorptions in the N-H and N-CH₃ regions. No monoradical impurities are observed and we attribute the hyperfine structures to some species derived from biradical **1** which can be monomer, dimer, or polymer. Indeed, from the nmr measurements on monoradical,¹⁷ we can assume an equilibrium between monomer and dimer¹⁸ (or polymer). For instance, two biradicals **1** can dimerize at N-O centers to give a new species **9** as shown in Scheme III.

Scheme III



Further reaction with other biradicals may lead to a trimer or higher polymers. The fact that pure biradical **1** is diamagnetic in the solid state and very in-

(15) R. W. Kreilick, *Mol. Phys.*, **14**, 495 (1968); *J. Amer. Chem. Soc.*, **90**, 2711 (1968). Kreilick introduced the use of stable di-*t*-butyl nitroxide free radical as a spin relaxer to narrow nmr lines of paramagnetic compounds in solutions at low concentration. We prefer to use *N*-oxytetramethyloxazolidine because it is easier to prepare. See J. K. W. Keana, S. B. Keana, and D. Beetham, *J. Amer. Chem. Soc.*, **89**, 3055 (1967); R. Chiarelli and A. Rassat, *Tetrahedron*, **29**, 3639 (1973).

(16) A. Rassat and P. Rey, *Tetrahedron*, **29**, 1599 (1973).

(17) R. M. Dupeyre, A. Rassat, and J. Ronzaud, to be submitted for publication.

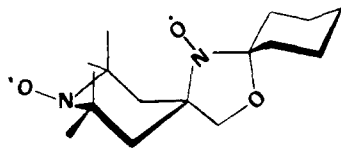
(18) G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6390 (1973).

(19) This is another case of positive and negative γ hfsc's¹¹ for protons attached to a same carbon atom.

(20) See its synthesis in the Experimental Section. We have synthesized this cognate nitroxide since the methyl groups on bridgehead positions prevent dimerization.¹¹

soluble may be attributed to this polymerization. Dimers or polymers have a weak dipolar interaction (when the $\text{N}-\dot{\text{O}}\cdots\text{N}-\dot{\text{O}}$ distance is larger than 10 Å, D is smaller than 30 G) and probably a weak exchange energy. Their esr spectrum may then be similar to the esr spectrum of monoradicals²¹ (i.e., a three-line spectrum) except for a slightly larger line width, owing to dipolar relaxation. The poorly resolved experimental esr spectrum of biradical **1** at 100°, is similar to a calculated spectrum,²² with five components of Lorentzian line shape having 1:2:3:2:1 relative intensities, separated by $a_N/2 = 9.5 \pm 0.5$ G and an individual line width of about 10 G. Such a spectrum is consistent with a nitroxide biradical having an exchange energy much larger than the hyperfine splitting constant a_N (here measured as about 19 G).²³ On this basis, we assign the observed spectrum (Figure 2b) to biradical **1** as a monomer.

A question now arises: in spite of the expected large dipolar interaction ($\text{N}-\dot{\text{O}}\cdots\text{N}-\dot{\text{O}} \simeq 5$ Å: then $D \simeq 250$ G), can the esr spectrum of biradical **1** monomer in solution (0.002 M) show hyperfine structures? In the same conditions as for biradical **1**, the nondimerizing nitroxide biradical **10**^{3e} taken for comparison since it



(10)

has the same dipolar interaction ($D \simeq 230$ G) only shows an esr spectrum consisting of a single broad line of ca. 30 G width. This line can be reproduced with five Lorentzian components, shape of 1:2:3:2:1 relative intensities, and an individual line width $\Delta H \simeq 15$ G.

For a biradical with large dipolar splitting D , dipolar relaxation is the main line-broadening mechanism.²³ In the fast tumbling limit, line width is approximately proportional to the hydrodynamic volume of the biradical.^{23c} Molecular models show that biradical **1** being almost spherical it is less bulky than biradical **10**. It seems reasonable to expect (at the same temperature and in the same solvent) an individual line width Δh of biradical **1** to be smaller than the individual line width ΔH of biradical **10**, i.e., $\Delta h < 15$ G. The hyperfine structure observed in solution at 100° can safely be attributed to biradical **1** as a monomer, in spite of its large dipolar splitting. The changes in esr spectrum observed after dissolution are attributed to the dissolution of the "polymeric solid" into some dimer or polymer in solution, giving finally at 100°, in

(21) R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

(22) Ya. S. Lebedev, "Atlas of ESR Spectra," Consultants Bureau, New York, N. Y., 1964.

(23) (a) N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.*, 73, 679 (1948); (b) R. Kubo in "Fluctuation, Relaxation and Resonance in Magnetic Systems," D. Ter Haar, Ed., Oliver and Boyd, Edinburgh, 1962, p 23; (c) J. Michon and A. Rassat, *J. Amer. Chem. Soc.*, 96, 335 (1974).

sufficiently dilute solution (0.002 M), biradical **1** as a pure monomer.

(III) Interpretation of the ESR Spectra of the N,N' -Dioxy-2,6-diazaadamantane Biradical in Frozen Solution²⁴

(1) **Dipolar Interaction in Biradical 1.** (a) **Measurements.** The theoretical " $\Delta m = 1$ " spectrum given in ref 25 for a zero-field tensor with axial symmetry is similar to our experimental spectrum if the hyperfine splittings are ignored (Figure 3a). The central line of this spectrum is assigned to the dimeric or polymeric species derived from biradical **1** and formed during freezing of the solution. In fact by successive dilutions the intensity ratio between the triplet part of the spectrum and the central line changes. Neglecting this central line we can accurately measure D parameter by choosing the peaks of $B \parallel Z$ absorption: $|D| = 250$ G = 710 MHz = 0.0240 cm^{-1} . This value agrees with that obtained from the central line of the equally spaced singularities observed on the two other peaks ($B \perp Z$).

(b) **Two Simple Descriptions of Biradical 1.** Because the diazaadamantane biradical is composed of light atoms, we attribute the zero field effects to dipolar spin-spin interaction only.²⁶ We assume that biradical **1** like monoradicals **5** and **7** has bent nitroxide groups in "fast" inversion. Consequently, we shall consider the nitroxide groups of biradical **1** as planar. Then owing to the D_{2d} symmetry of the molecule, the electron spin-spin coupling D tensor and the g_e tensor possess cylindrical symmetry about the $\text{N}-\dot{\text{O}}\cdots\text{N}-\dot{\text{O}}$ line noted as Z axis. When developed in the principal axes X , Y , and Z of D tensor (second rank), the Zeeman and dipolar interactions will be described by the spin Hamiltonian ($S = 1$)

$$\mathcal{H}_t = \beta_e B g_e S + \frac{1}{2} SDS = \beta_e B g_e S + D(S_z^2 - (S^2/3))$$

where $D = \frac{3}{4} D_{zz}$. For a two-electron triplet state described by the function $\psi_T(1,2)$, D_{zz} is simply equal to

$$D_{zz} = g_e^2 \beta_e^2 \left\langle \psi_T(1,2) \left| \frac{r_{12}^2 - 3z_{12}^2}{r_{12}^5} \right| \psi_T(1,2) \right\rangle$$

r_{12} is the vector connecting electrons 1 and 2, z_{12} is its component along Z axis. All the other parameters have their usual meaning.² In principle, it should be possible to use the experimental data on D tensor to determine the $\dot{\text{O}}-\text{N}\cdots\text{N}-\dot{\text{O}}$ distance with an appropriate triplet wave function. But this theoretical determination involves multicenter integrals which are difficult to calculate.²⁷

Since this molecule has a simple rigid skeleton, we have preferred to use our data to check two simple descriptions of a bisnitroxide. Indeed, it has been shown that due to the antisymmetry of the space part of the wave function in the triplet state, the zero-field

(24) A referee suggested a single crystal study of **1** in diamagnetic host. Actually, we have tried such a study but the low solubility of **1** does not allow the growing of crystals sufficiently doped to be observed by esr.

(25) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, 41, 1763 (1964).

(26) (a) M. F. Hameka and L. J. Oosterhoff, *Mol. Phys.*, 1, 358 (1958); (b) S. J. Fogel and M. F. Hameka, *J. Chem. Phys.*, 42, 132 (1965).

(27) G. De Jager, J. De Jong, C. Mc Lean, and P. Ros, *Theor. Chim. Acta*, 20, 57 (1971), and references cited therein.

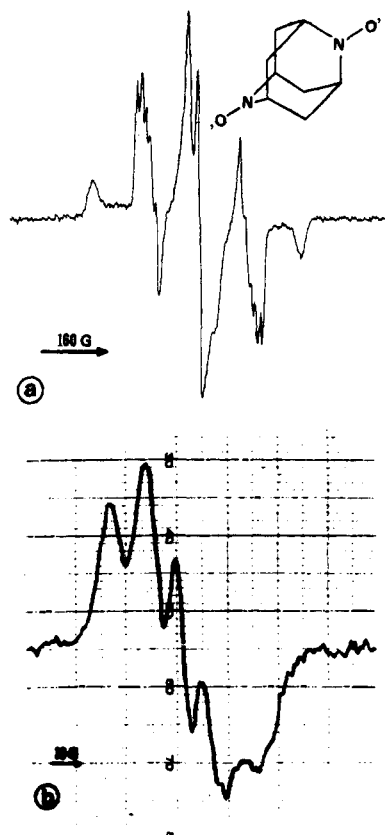


Figure 3. (a) ESR spectrum " $\Delta m = 1$ " of a solution (0.002 M) of biradical **1** in DMF at liquid nitrogen temperature. (b) " $\Delta m = 2$ " corresponding absorption.

splittings contain no contribution from close approach of electrons.²⁸ The calculated values are then not very sensitive to fine details of the spin distribution. Therefore approximate wave functions are sufficient to estimate the zero-field splittings.²⁹

Let us assume that biradical can be adequately described as a system of two centers A \cdots B and two electrons. The dipolar magnetic system of the diazaadamantane biradical then consists of two opposite nitroxide groups on the same N,N-axis having perpendicular π orbitals, each orbital containing one unpaired electron (Figure 4).

The simplest approximation is the point dipole approximation, where we write that $z_{12} = r_{12} = R_{AB}$ in the expression of D_{zz} . The R_{AB} distance calculated in this way is 4.8 Å which is the distance measured on molecular models between the middles of the two N-O bonds.

A more elaborate approximation is the Heitler-London approximation.³⁰ The triplet wave function $\psi_T(1, 2)$ is then

$$\psi_T(1, 2) = \frac{1}{\sqrt{2}} (\pi_A^*(1)\pi_B^*(2) - \pi_A^*(2)\pi_B^*(1))$$

where π_A^* and π_B^* are the antibonding π molecular orbitals of the two unpaired electrons on each N-O group. For a N-O group K (A or B), in the simple

(28) H. M. McConnell, *Proc. Nat. Acad. Sci. U. S.*, **45**, 172 (1959).

(29) A. Pulman and E. Kochanski, *Int. J. Quantum Chem.*, **1**, 25 (1967).

(30) J. C. Slater, "Quantum Theory of Molecules and Solids," Vol. 1, McGraw-Hill, New York, N. Y., 1965, p 49.

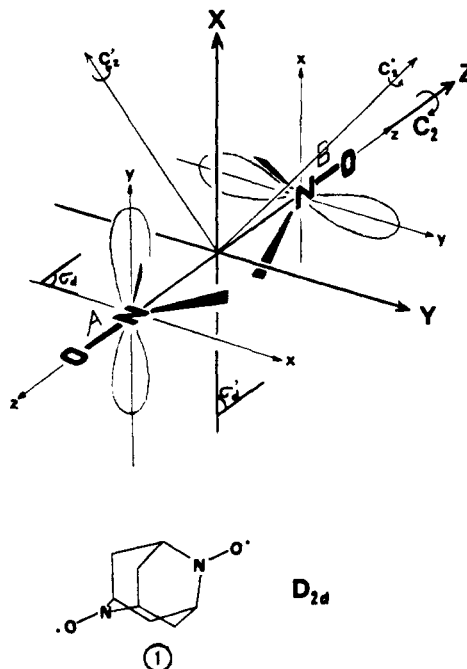


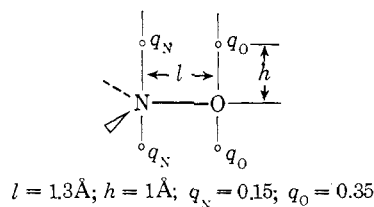
Figure 4. Hyperfine electron-nitrogen anisotropic coupling A_A and A_B tensors located with respect to the axially symmetrical dipolar magnetic D tensor of biradical **1**.

LCAO description, the antibonding molecular orbital π_K^* is

$$\pi_K^* = \sqrt{\lambda}(2p_{v_{N_K}}) - \sqrt{(1-\lambda)}(2p_{v_{O_K}})$$

where λ and $1 - \lambda$ are the electron populations ρ_{N_K} and ρ_{O_K} respectively in the $2p_y$ orbitals of N_K and O_K atoms. A good evaluation²⁹ of the integral representing D is to calculate in its development the two-center coulomb type terms only. It is a simplification to describe the $2p_{v_{N_K}}$ atomic orbitals by two half-charges $q_i = 1/2\rho_i$ located at a distance h above and below the plane containing the atom i ($i = N$ or O). We have chosen the following parameters: charges q_i from the *ab initio* calculated electron populations ρ_i in aminoxy radical,³¹ $q_N = 0.135$ and $q_O = 0.365$; N-O bond length from X-ray measurements,³² mean value is 1.29 Å; N \cdots N distance from molecular models, $d = 3.2$ Å.

The best fit to the experimental value of D is obtained when the parameter h is equal to 0.6 Å.³³ This seems to be an appropriate description of saturated nitroxides for dipolar problems and the following parameters can be used.



(31) Y. Ellinger, Thesis, Grenoble, 1973.

(32) See ref 1 and quoted reference.

(33) A similar quadrupole description of the N-O group has been used to rationalize the proton nmr shifts on *N*-oxy-2,2,6,6-tetramethylpiperidino single crystal at low temperature. Good agreement with experiment is found for $q_N = 0.15$ and $h = 1.2$ Å. F. Ferrieu and M. Nechtschein, *Chem. Phys. Lett.*, **11**, 46 (1971).

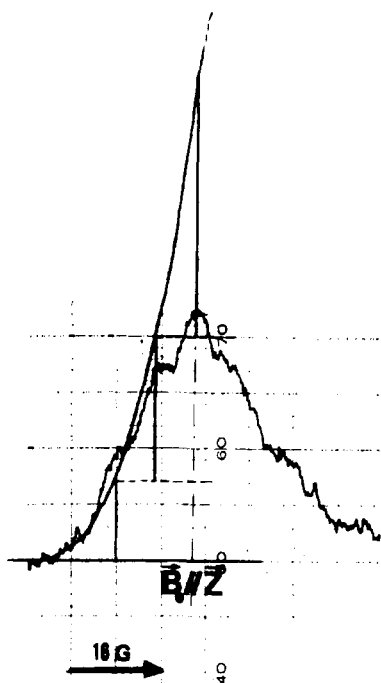


Figure 5. Hyperfine structures on the dipolar fine structure (Figure 3a) corresponding to the canonical resonance field $B_0 \parallel Z$. The solid line ending in dashes represents the integral of the half-fine structure.

(2) **Hyperfine Structures in Dipolar “ $\Delta m = 1$ ” Spectrum of Biradical 1.** (a) **Simplifications for the Analysis of the Spectrum.** In order to account for the hyperfine lines present in the esr spectrum, we introduce a spin Hamiltonian \mathcal{H}_{hf} consisting of exchange, hyperfine, and nuclear Zeeman terms³⁴

$$\mathcal{H}_{\text{hf}} = J s_1 s_2 + s_1 \mathbf{A}_A i_A + s_2 \mathbf{A}_B i_B - g_N \beta_N B i_A - g_N \beta_N B i_B$$

where s_1 , s_2 , i_A and i_B refer respectively to the unpaired electron spins and to the two nitrogen nuclear spins. All the parameters have their usual meaning.² We assume hyperfine electron–nitrogen anisotropic coupling \mathbf{A} tensors to be axially symmetrical along the $2p_y$ orbital of the nitrogen nucleus.³⁵ Then the components of \mathbf{A} tensors are $a + 2b$ along the $2p_y$ orbital and $a - b$ along the other axes; a is the isotropic coupling constant; a and b have positive signs.³⁶ It is now easy to locate \mathbf{A}_A and \mathbf{A}_B tensors with respect to \mathbf{D} and \mathbf{g}_e tensors (Figure 4): all tensors have parallel principal axes. The molecular axes are taken as the two perpendicular “ $2p_y$ orbitals” (X and Y axes) and $\text{N} \cdots \text{N}$ line (Z axis). Expansion of the following spin Hamiltonian (X, Y, Z molecular axes)

$$\mathcal{H}_1 = \mathcal{H}_f + J s_1 s_2 = \beta_e B g_e S + D(S_z^2 - \frac{1}{3} S^2) + (J/2) S^2 - 3(J/4)$$

(with $S = s_1 + s_2$) in the singlet $|S_0\rangle_W$ and triplet $|\Sigma_{+1}\rangle_W$, $|\Sigma_0\rangle_W$, $|\Sigma_{-1}\rangle_W$ functions gives to zeroth order

(34) D. C. Reitz and S. I. Weissman, *J. Chem. Phys.*, **33**, 700 (1960).

(35) (a) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965); (b) see ref 2a.

(36) (a) E. Kochanski and G. Berthier, “La structure hyperfine des Atomes et des Molecules,” colloque CNRS, Paris, 1966; (b) see ref 2a.

($D \ll 2g_e \beta_e B$) the singlet and triplet energy levels (we make the convenient change of axes (X, Y, Z) \rightarrow (U, V, W) by choosing the external magnetic field B as rotating quantization W axis).³⁷ Inclusion of ^{14}N hyperfine interactions by the Hamiltonian $\mathcal{H}_2 = s_1 \mathbf{A}_A i_A + s_2 \mathbf{A}_B i_B - g_N \beta_N B i_A - g_N \beta_N B i_B$ changes the 4×4 matrix of \mathcal{H}_1 in the singlet–triplet representation into a 36×36 matrix of $\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2$ in the simple product representation with the nuclear states $|m_{iA}\rangle$ and $|m_{iB}\rangle$. It is possible to simulate the spectrum of biradical molecules oriented at random. However, a computer fit of the numerous spin hamiltonian parameters [\mathbf{g}_e , \mathbf{A}_A , \mathbf{A}_B , \mathbf{D} , J , and $B(\Omega)$, Ω being the set of three orientation parameters] could have been too time consuming. It is known that the $\Delta m = 1$ transitions of an ensemble of triplets oriented at random are distinguishable only in the canonical orientations³⁹ and the spectrum possesses the same properties as the spectrum of an assembly of these triplets in a host crystal.⁴⁰ We have therefore attempted to derive from the experimental spectrum the values of hyperfine parameters by rationalizing the observed hyperfine splittings for the two canonical orientations of the magnetic field B : where B is parallel and perpendicular to the great axis Z of \mathbf{D} tensor.

(b) (i) **Measurements along the Canonical Resonance Field $B_0 \parallel Z$.** Five singularities, equally spaced of 13 G, are observed on each dipolar $B_0 \parallel Z$ fine structure with relative intensities 1:2:3:2:1 (Figure 5).

The interpretation of this hyperfine spectrum is straightforward. B being parallel to a common principal axis of the three \mathbf{A}_A , \mathbf{A}_B , and \mathbf{D} tensors, all off-diagonal terms of the matrix \mathcal{H} are zero and the structure of the spectrum will depend, to zeroth-order, only upon the possibility of singlet–triplet mixing in a given nuclear spin multiplicity through the magnitude of the ratio between exchange and hyperfine energies. The two components $A_{A_{\parallel}}$ and $A_{B_{\parallel}}$ of hyperfine tensors are both equal to $a - b$. The five observed equally spaced singularities with relative intensities 1:2:3:2:1 suppose an exchange energy J such that $|J| \gg |a - b + (2D/3)| \simeq |2D/3|$. Then separation between lines is equal to $(a - b)/2$. Experimentally we must conclude that $|J| \gg 170 \text{ G} = 470 \text{ MHz}$ and $|2(a - b)| = 26 \text{ G}$.

(ii) **Measurements along the Canonical Resonances Fields $B_0 \perp Z$.** Five singularities, nonequally spaced, are observed on each dipolar $B_0 \perp Z$ fine structure whose half-width is 25 G (Figure 6a).

When B_0 rotates in the XY plane with an angle ω between B_0 and X axis, B_0 is not always parallel to the principal axis of the \mathbf{A}_A and \mathbf{A}_B tensors, except in the X and Y directions, and off-diagonal terms are not always negligible. In order to account for this, we neglect first the nuclear Zeeman energies and introduce the two electron fields B_1 and B_2 having for origin the electron spins s_1 and s_2 acting upon i_A and i_B through spin–spin interactions.

By quantization of nuclear spins i_A and i_B respectively

(37) $|\Sigma\rangle_W$ eigenstates are linear combinations of the usual basic triplet functions $|T_{+1}\rangle_Z = \alpha(1)\alpha(2)$, $|T_0\rangle_Z = (1/\sqrt{2})(\alpha(1)\beta(2) + \beta(1)\alpha(2))$, and $|T_{-1}\rangle_Z = \beta(1)\beta(2)$ which diagonalize S^2 and S_z , using the rotation operator.³⁸

(38) M. F. Rose, “Elementary Theory of Angular Momentum,” Wiley, New York, N. Y., 1967, p 48.

(39) The term canonical orientations refers to magnetic field alignments such that B is parallel (or nearly parallel) to one of the principal molecular axes.

(40) P. Kottis, *Ann. Phys. (Paris)*, **4**, 459 (1969).

along B_1 and B_2 , \mathcal{H}_2 is simply equal to $s_{1w}A_A'i_{A_{B_1}} + s_{2w}A_B'i_{B_{B_2}}$, with

$$A_A' = [9b^2 \sin^2 \omega \cos^2 \omega + (a - b(1 - 3 \cos^2 \omega))^2]^{1/2}$$

$$A_B' = [9b^2 \sin^2 \omega \cos^2 \omega + (a - b(1 - 3 \sin^2 \omega))^2]^{1/2}$$

Fast exchange condition $|J| \gg |a - (b/2) + (D/3)| \approx |D/3|$ is already fulfilled since we know that $|J|$ is greater than $|2D/3|$: singlet and triplet states are not mixed. The spin Hamiltonian \mathcal{H} is then, to zeroth order, diagonal in the $|\Sigma\rangle_w |m_{iA}\rangle |m_{iB}\rangle$ basis functions. Calculation of absorption lines is straightforward. We may observe on each dipolar $B_0 \perp Z$ fine structure an accumulation of equally probable hyperfine spectra, which are similar to spectra observed when one electron interacts with two nitrogen nuclei $^{14}\text{N}_A$ and $^{14}\text{N}_B$. The hyperfine constants are $1/2 A_A'$ and $1/2 A_B'$. Figure 6b shows, for reasonable values of a and b (we know that $|a - b| = 13$ G and $a, b > 0$), the stick diagrams obtained by accumulation of calculated half-spectra ($0 \leq \omega \leq 45^\circ$, for symmetry reason) ($\delta\omega = 5^\circ$), using an "accumulation step" of 2 G for an experimental spectrum width of about 60 G. Considering now the nuclear Zeeman energies, additional satellite lines appear because of "forbidden" transitions in which both electron and nuclear spins "turn over." Added to the natural line width, to a slightly anisotropic g_e factor, to the contributions of all other molecules which have the magnetic field outside the XY plane and which consequently cause absorption in the entire region of the hyperfine spectrum of concerned molecules (B_0 in XY plane), all these parameters drastically decrease the expected resolution of the hyperfine spectrum. Fortunately, the first derivative of the absorption line may be regarded as infinite at the canonical resonance fields. This allows ready detection of peaks which create singularities in the envelope of their overall hyperfine spectrum. Among the possible stick diagrams of Figure 6b, we choose one which shows characteristics similar to the experimental spectrum: five singularities, with graphically estimated relative intensities 1:2.4:2.2:2.4:1 and with the same half-width (peak to peak = 25 G) (Figure 6a). The hyperfine parameters thus evaluated, $|A_N^{xz}| = |A_N^{zz}| = |a - b| = 13$ G and $|A_N^{yy}| = |a + 2b| = 34$ G are consistent with other determinations for the nitroxide group.⁴¹ Furthermore, the isotropic hyperfine coupling constant a_N thus evaluated in DMF, 20 ± 0.5 G, is equal to that measured in dilute solution and attributed to biradical **1**. This large value is characteristic of a bridged nitroxide group (see monoradicals **5** and **7** and ref 10).

The symmetry properties of the rigid skeleton of the diazaadamantane dinitroxide, the particular selecting properties of the high field spectrum of its glassy solution, and a dipolar parameter sufficiently large to avoid overlapping of fine structures have allowed a consistent analysis of the esr spectrum without aid of spectrum synthesis. It is true that the hyperfine splittings observed in frozen solutions are not accurate enough to warrant the slight advantage afforded by spectrum reproduction over the approximate analysis.

(41) A. R. Forrester, J. M. Hay, and R. M. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, London, 1968; I. Smith, "Application of Electron Spin Resonance Spectroscopy," J. R. Bolton, D. Borg, and H. Swartz, Ed., Wiley, New York, N. Y., 1971.

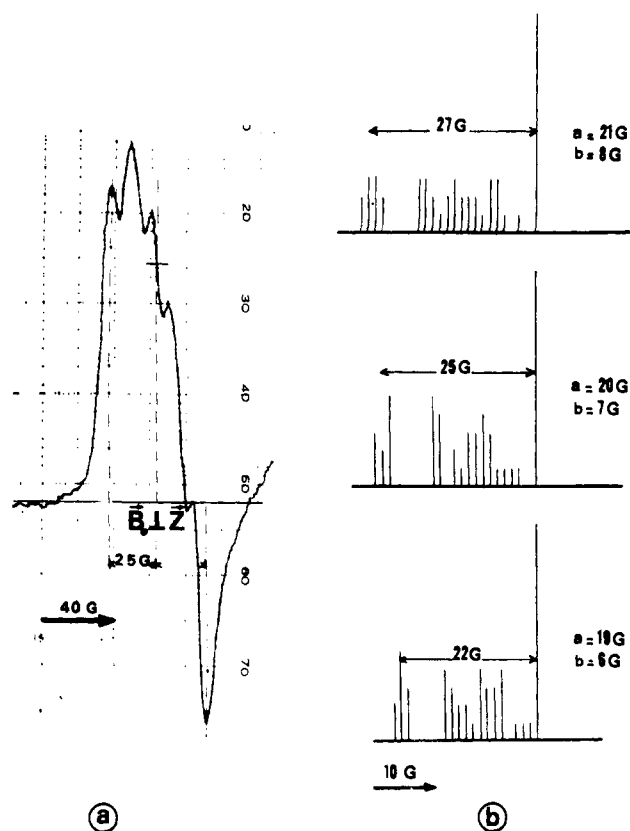


Figure 6. (a) Hyperfine structures on the dipolar fine structure (Figure 3a) corresponding to the canonical resonance fields $B_0 \perp Z$. (b) Stick diagrams representing the accumulation of calculated hyperfine half-spectra, when the resonance field B_0 rotates in the plane perpendicular to Z axis (see text).

(3) Exchange Energy J of Biradical **1.** The exchange energy J introduced in the spin Hamiltonian is the separation between the two lowest singlet and triplet states⁴² of the biradical. It is of physical importance to know the magnitude and sign of J , *i.e.*, whether this biradical has a singlet or triplet ground state.

(a) Measurement. We have deduced J from the temperature dependence of the intensity I of the " $\Delta m_s = \pm 2$ " transition line (Figure 3b), in *o*-terphenyl glass. The intensity has been fitted to the theoretical expression.⁴³

$$I = \frac{C}{T^3 + e^{J/T}}$$

where C is a constant depending upon experimental conditions. Best fit is obtained for $J = -170^\circ\text{K}$, standard deviation = 15°K . Biradical **1** is then a *ground state triplet*. The triplet-singlet separation is $|J| = 0.3$ kcal/mol = 110 cm⁻¹ = 3×10^6 MHz.

(b) Interpretation. When two monoradicals (doublet states) are in interaction (*e.g.*, biradicals in dilute solution), we expect singlet and triplet electronic manifolds. Will the electronic ground state be singlet or triplet? For two interacting atoms giving a diatomic molecule, Hund's rule is verified, we obtain a singlet ground state⁴⁴

(42) P. O. Lowdin, *Rev. Mod. Phys.*, **34**, 80 (1962).

(43) B. Bleaney and D. K. Bowers, *Proc. Roy. Soc., Ser. A*, **214**, 451 (1952).

(44) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, Van Nostrand, New York, N. Y., 1950, pp 502-579.

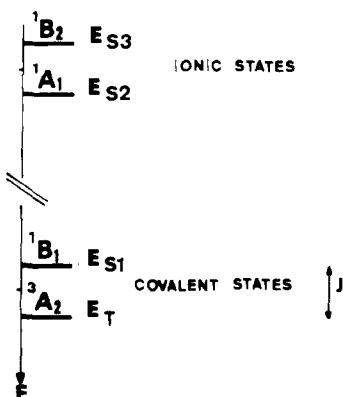


Figure 7. Energy diagram of biradical **1** described as a pseudo- H_2 molecule.

except in cases of orbital degeneracy as in the O_2 molecule.⁴⁵ What is the case for biradical **1**? Is it possible to predict a ground state triplet on the basis of D_{2d} symmetry? We shall examine the different predictions according to different models of the biradicals.

(A) If biradical **1** is described as a pseudo H_2 molecule, $A \cdots B$ with two orthogonal (D_{2d} symmetry) orbital functions π_A^* and π_B^* as previously defined, we can build up six functions of proper symmetry: a threefold degenerate triplet covalent state 3A_2 and three singlet states; a covalent 1B_1 state and two ionic 1A_1 and 1B_2 states. In the expression of $J = E_T - E_S$, there are no contributions from kinetic and potential energies. $-J$ is then equal to the electrostatic repulsion energy, which is definitively positive. If we introduce some delocalization of the electrons from one of the N- \dot{O} centers to the other one,⁴⁶ we modify drastically the magnitude of J (the one-center integrals are large) without changing its sign. Thus, with the $A \cdots B$ model of the biradical, the ground state is always the triplet state (Figure 7).

(B) If biradical **1** is described as two dimerizing nitroxide radicals in the D_{2d} symmetry, we can build the MO energy level scheme (Figure 8), using the 20 valence atomic orbitals of the $H_4N_2O_2$ dimer as a basis. The 20 LCAO molecular orbitals (MO) representation is reduced to $5A_1 + 5B_2 + 5E$. By comparison⁴⁷ with a valence bond description of the dimer, these MO's can be classified into six σ bonding MO's ($3A_1 + B_2 + E$), a doubly degenerate π bonding MO (E), four n nonbonding MO's ($A_1 + B_2 + E$) arising from the lone-pair electrons of oxygen atoms, a doubly degenerate π^* antibonding MO (E), and six σ^* antibonding MO's ($A_1 + 3B_2 + E$). We assume that the antibonding π^* energy levels lie between the σ or π or n energy levels and the antibonding σ^* energy levels. According to the "Aufbau Principle," we must fill the doubly degenerate π orbital with only two electrons (Figure 8). As long as spin-orbit coupling is small (to interpret the fine structures in the esr spectrum of the biradical, we have neglected spin-orbit coupling), such an $(e)^2$ electron configuration of a species of D_{2d} symmetry gives again three 1A_1 , 1B_1 , and 1B_2 singlet states and one 3A_2 triplet state.⁴⁸ Now, if Hund's rule can be applied

(45) See ref 30, pp 117-127.

(46) See the Coulson-Fisher method of treating the H_2 molecule in ref 30, pp 71-74.

(47) H. B. Thompson, *Inorg. Chem.*, **7**, 604 (1968).

(48) See ref 44, Vol. 3, p 332.

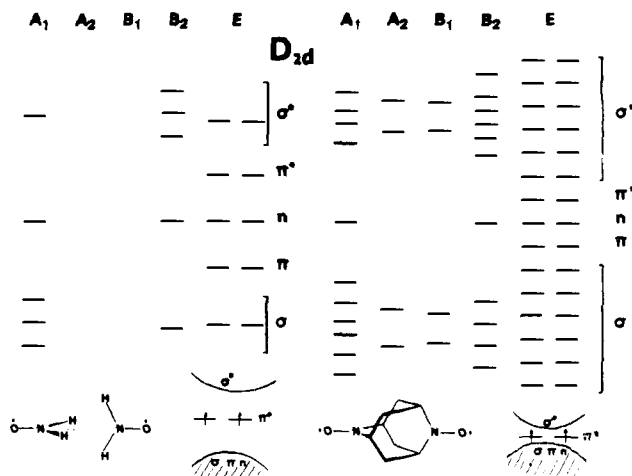


Figure 8. *Left*: molecular orbitals diagram of biradical **1** described as a system consisting of two elementary nitroxide radicals dimerizing in the D_{2d} symmetry group. *Right*: expected molecular orbitals diagram of biradical **1**.

to polyatomic molecules as well as to atoms and diatomic molecules,⁴⁵ the simple MO theory leads to a ground state triplet.

(C) If we deal now with the total molecule, in the same molecular orbital description, we shall assume that the introduction of the carbon and proton framework will make a compression of the bonding and antibonding MO levels (Figure 8) relative to the dimer model B. If so, the conclusions of the previous model then remain valid.

Under these assumptions, the fact that biradical **1** is a ground state triplet may be attributed to its D_{2d} symmetry.

(4) *g* Values of Biradical **1**. On the frozen solution esr spectrum of biradical **1** (Figure 3a), the two principal parameters of the g_e tensor (second rank) can be measured: $g_{||} = 2.0097 \pm 0.0005$ and $g_{\perp} = 2.0060 \pm 0.0005$. Principal values of the g_e tensor have been measured for various nitroxide monoradicals.⁴⁹ From these values, it is expected that in biradical **1** $g_{||} \approx g_{zz} = 2.01 \pm 0.005$ and $g_{\perp} \approx \frac{1}{2}(g_{xx} + g_{yy}) = 2.0045 \pm 0.001$. There is good agreement between the experimental and the expected $g_{||}$ values. On the other hand, the experimental g_{\perp} value is slightly different from the expected value. If this variation is significant, it may be evidence for a slight increase of the spin-orbit coupling⁵⁰ in case of biradical **1** compared to cases of nitroxide monoradicals of lower symmetry; due to D_{2d} group symmetry of biradical **1**, numerous configurations of E symmetry can be found among the first excited states; these E configurations give rise to contributions to g_{\perp} . Although they may be weak, they are probably sufficient to make g_{\perp} larger than the expected value.

(49) (a) O. H. Griffith, D. W. Cornell, and H. M. McConnell, *J. Chem. Phys.*, **43**, 2909 (1965); (b) see ref 2a; (c) W. L. Hubbell and H. M. McConnell, *Proc. Nat. Acad. Sci. U. S.*, **64**, 20 (1969); (d) B. G. McFarland and H. M. McConnell, *ibid.*, **68**, 1274 (1971); (e) P. Jost, L. J. Libertini, V. C. Hebert, and O. H. Griffith, *J. Mol. Biol.*, **59**, 77 (1971); (f) D. Bordeaux, J. Lajzerowicz-Bonneteau, R. Briere, H. Lemaire, and A. Rassat, *Org. Magn. Resonance*, **5**, 47 (1973); (g) L. I. Antsiferova, N. S. Nazemets, and N. V. Rabin'kina, *Mol. Phys.*, **25**, 909 (1973).

(50) The deviation Δg of the experimental g factors from the free electron g_e value are attributed to spin-orbit coupling: A. J. Stone, *Mol. Phys.*, **6**, 509 (1963).

Conclusions

The high symmetry of *N,N'*-dioxy-2,6-diazaadamantane, probably the simplest and the most symmetrical stable nitroxide biradical, is reflected in its magnetic properties: the observed hyperfine structures on its esr spectrum in solution have been interpreted as a feature of *its almost spherical shape*; the analysis of the hyperfine structures of its esr spectrum in frozen solution has been made easy because of *the coincidence of the principal axes of all the various magnetic second rank tensors*; finally it is possible to rationalize, on the basis of *the D_{2h} symmetry* having one degenerated representation, the slight "anomaly" found for g_{\perp} and the fact that biradical **1** is a ground state triplet.

Experimental Section

Pseudopelletierine, 2. Prepared according to the directions of Cope, Dryden, and Howell;⁵¹ mp 64° (lit.⁵² mp 64–65°) after recrystallization from petroleum ether. The infrared spectrum of **2** shows characteristic peaks at 1710 cm⁻¹ (C=O): nmr (CCl₄) δ 2.5 (3 H), 3.15 (2H), multiplet 2.2 (4 H), broad line 1.6 ppm (6 H).

3- α -Benzylaminopseudopelletierine, 3a. A solution of 15.3 g of pseudopelletierine (0.1 mol), 10.7 g of benzylamine (0.1 mol), and 24.4 g of *p*-toluenesulfonic acid in 200 ml of benzene was refluxed under a water separator. After 15 hr the theoretical amount of water was collected (0.1 mol). After removal of the solvent, the oil obtained was added to 150 ml of methanol and hydrogenated in the presence of 1 g of Adams platinum oxide. The mixture was heated to 50° to initiate hydrogenation which then proceeded to completion in 4 hr. The catalyst and solvent were removed. The solid was dissolved in water and the solution was rendered strongly alkaline with sodium hydroxide. The oil was extracted by methylene chloride and dried and the solvent removed.

After chromatography on neutral alumina, we obtained 18 g of **3a** as a colorless oil (yield 74%): nmr (CD₂Cl₂) δ 2.35 (3 H), 2.9 (2 H), broad line at 1.5 (10 H), 3.7 (2 H); 7.2 ppm (5 H). This substance formed a dipicrate in methanol, which melted at 245°, after recrystallization from methanol. *Anal.* Calcd for C₁₆H₂₄N₂, 2(C₆H₃N₃O₇): C, 47.9; H, 4.27; N, 15.96; O, 31.9. Found: C, 47.83; H, 4.24; N, 15.94; O, 31.96.

***N*-Methyl-*N*-benzyl-2,6-diazaadamantane, 4.** A mixture of 3- α -benzylaminopseudopelletierine, **3a** (5.2 g), in cyclohexane (100 ml) and 12% sodium hydroxide (15 ml) was treated with a solution of bromine (1 ml) in cyclohexane (150 ml) added dropwise over 1.5 hr. During the addition the mixture was cooled in an ice bath. The cyclohexane solution of bromoamine **3b** was separated and the aqueous layer extracted with 20 ml of cyclohexane. The extracts were combined, washed with 12% sodium hydroxide (50 ml), and dried over anhydrous sodium sulfate. The cyclohexane was removed under reduced pressure. We obtained 6.5 g of *N*-bromoamine, yield 94%.

The *N*-bromoamine, **3b**, was dissolved in 70 ml of cold 84% sulfuric acid (80 ml of concentrated sulfuric acid, 20 ml of water). The solution was then heated at 65–70° during 30 min. After cooling, the mixture was added to 200 ml of ice-water, rendered strongly alkaline with 50% sodium hydroxide solution, and then extracted with methylene chloride. Drying over sodium sulfate, followed by solvent evaporation, yielded about 4 g of viscous oil.

A chromatography on 400 g of alumina gives 2.35 g of **3a** and 1.3 g of **4** (yield 25%). This substance **4** formed a dipicrate in methanol which melted at 260° after recrystallization: nmr (CD₂Cl₂) δ 2.4 (3 H), broad peak at 2.9 (4 H), broad peak at 1.9 (8 H), 3.9 (2 H), 7.2 ppm (5 H). *Anal.* Calcd for C₁₆H₂₂N₂, 2(C₆H₃N₃O₇): C, 48.00; H, 4.03; O, 31.97; N, 16.00. Found C, 48.03; H, 4.19; O, 31.86; N, 15.75.

2-Methyl-2,6-diazaadamantane, 6. *N*-Methyl-*N*-benzyl-2,6-diazaadamantane, **4** (830 mg), in 60 ml of ethanol was hydrogenolyzed in the presence of 10% palladium on charcoal at 70 atm and 75° during 6 hr. The catalyst was filtered and the solvent removed under reduced pressure. We obtained 500 mg of **6** (96% yield), mp 152°. This substance **6** formed a dipicrate in methanol which

melted at 308° after recrystallization. The infrared spectrum of **6** shows a characteristic peak at 3400 cm⁻¹ (N–H): nmr (CDCl₃) δ 1.95 (8 H), 2.5 (3 H), 2.85 (2 H), 3.45 (2 H), 4.4 ppm (1 H).

2,6-Diazaadamantane, 8. Following the procedure of Ciamician and Silber,⁵³ 1.5 g (0.008 mol) of potassium permanganate in 150 ml of water was added dropwise during 45 min, while stirring, to a solution of 0.5 g (0.002 mol) of *N*-methyl-*N*-benzyl-2,6-diazaadamantane, **4**, and 1.5 g of sodium hydroxide in 25 ml of water. The reaction mixture was maintained at 0–5° during the addition. After stirring during 40 hr, the mixture was filtered. The solution was acidified with 10% hydrochloric acid and the mixture concentrated under vacuum. The crude hydrochloride salt of **8** was treated with a solution of sodium hydroxide to liberate the base which was then isolated by methylene chloride extraction. We obtained 250 mg of diamine **8** (yield 80%), mp 240° (lit.⁵⁴ 238°). *Anal.* Calcd for dipicrate C₈H₁₄N₆, 2(C₆H₃N₃O₇) (mp 320°): C, 40.28; H, 3.35; O, 37.46; N, 18.80. Found: C, 40.42; H, 3.55; O, 37.28; N, 18.75. The infrared spectrum shows characteristic peaks at 3350 cm⁻¹ (N–H): nmr (C₆D₆) δ 1.7 (8 H), 3 (4 H), 4.5 ppm (2 H).

***N,N'*-Dioxy-2,6-diazaadamantane, 1.** (a) **By Oxidation with Potassium Permanganate of 4.** Potassium permanganate (4 g) in 220 ml of water was added dropwise during 45 min, while stirring, to a solution of 1 g of *N*-methyl-*N*-benzyl-2,6-diazaadamantane, **4**, and 4 g of sodium hydroxide in 40 ml of water. The reaction mixture was maintained at 0–5° during the addition. After stirring over 1 week, the mixture was filtered and the filtrate extracted with methylene chloride. After removal of the solvent followed by chromatography on alumina, we obtained 220 mg of **1** (yield 31%) as yellow diamagnetic needles from chloroform, mp 240° dec, mass spectrum M 168. *Anal.* Calcd for C₈H₁₂N₂O₂: C, 57.13; H, 7.19; O, 19.03; N, 16.66. Found: C, 57.08; H, 7.13; O, 19.25; N, 16.52. The infrared spectrum shows no band in the absorption region 3,300 cm⁻¹ (N–H). The esr spectrum in the solid state shows a very weak absorption. In a frozen solution of dimethylformamide the esr spectrum is characteristic of dipolar interaction, $2D = 510$ G.

(b) **By Oxidation with Hydrogen Peroxide of 5.** To a solution of 30 mg of *N*-oxy-2,6-diazaadamantane, **5**, in 5 ml of water we added 1 mg of phosphotungstic acid and 60 μ l of 30% hydrogen peroxide. The reaction mixture was cooled in an ice bath. After stirring for 1 hr, the mixture was extracted by methylene chloride. The solvent was removed and yielded 25 mg of crude product which was then purified by chromatography on alumina. We obtained 20 mg of pure **1** (65% yield), mp 240°.

(c) **By Oxidation of Diamine 8 with Hydrogen Peroxide.** To a solution of 250 mg of **8** in 4 ml of water, we added 3 mg of phosphotungstic acid and 0.6 ml of hydrogen peroxide. The reaction mixture was cooled in an ice bath. After 15 min a yellow powder precipitate was formed. The mixture was filtered and oxidation of filtrate continued during 1 hr.

The yellow powder, 100 mg, was purified by chromatography on alumina and yielded 65 mg of biradical **1** (mp 240°) (yield 21%).

The filtrate was then extracted with methylene chloride. The solvent was dried over anhydrous sodium sulfate and then evaporated from the solution. We obtained 120 mg of crude product. A chromatography on alumina distinguished 10 mg of biradical **1**, 40 mg of monoradical **5** (yield 15%), and 40 mg of diamine **8**.

The monoradical **5**: yellow powder mp 192°; it shows characteristic peaks at 3200 cm⁻¹ (N–H); nmr (CD₂Cl₂) δ +2.05 G (2 H), +1.30 G (6 H), –0.75 G (4 H); esr spectrum (dilute solution in water saturated with lithium chloride) $a_N = 19.2$ G, $a_H = 2.80$ (2 H), 1.45 (6 H), 0.80 (4 H).

(d) **By Oxidation of Diamine 6 with Hydrogen Peroxide.** To a solution of 500 mg of *N*-methyl-2,6-diazaadamantane, **6**, in 6 ml of water was added 3 mg of phosphotungstic acid and 0.5 ml of hydrogen peroxide. The reaction mixture was cooled in an ice bath. After stirring for 1 hr, the mixture was extracted by methylene chloride. The solvent was removed and yielded 300 mg of crude yellow product. A chromatography on alumina distinguished 10 mg of biradical **1** and 25 mg of monoradical **7**, mp 204° (yield 5%); esr spectrum in benzene, three lines $a_N = 18.12$ G.

1,5,7-Trimethylnorpseudopelletierine, 11. Prepared by Robinson Schöpf condensation between 4-methyl-2,6-heptanedione,⁵⁵ ammonium chloride, and acetonedicarboxylic acid, according to the

(51) A. C. Cope, H. L. Dryden, Jr., and C. F. Howell, *Org. Syn.*, **4**, 816 (1963).

(52) A. C. Cope, H. L. Dryden, Jr., C. G. Overberger, and A. A. D'Addieco, *J. Amer. Chem. Soc.*, **73**, 3416 (1951).

(53) G. Ciamician and P. Silber, *Ber.*, **27**, 2850 (1894).

(54) H. Stetter and K. Heckel, *Tetrahedron Lett.*, **No. 19**, 1907 (1972).

(55) J. P. Schirmann and J. Dreux, *Bull. Soc. Chim. Fr.*, **10**, 3903 (1967).

process used to the syntheses of pseudopelletierine,⁵⁶ mp 65°. This substance formed a picrate in methanol, which melted at 270°. *Anal.* Calcd for C₁₁H₁₉NO, C₆H₈N₂O₇: C, 49.75; H, 5.40; N, 13.65; O, 31.39. Found: C, 49.89; H, 5.32; N, 13.46; O, 31.33. The infrared spectrum of **11** shows characteristic peaks at 3250 cm⁻¹ (N-H) and 1720 (cm⁻¹ (C=O); nmr (CD₂Cl₂) δ 1.2 ppm (6 H), multiplet 2.2 (4 H), 0.85 ppm (4 H).

1,5,7-Trimethylnorpseudopelletierine N-Oxyl, 12. To a solution of 1 g of 1,5,7-trimethylnorpseudopelletierine in 10 ml of water was added 10 mg of phosphotungstic acid and 1.2 ml of hydrogen peroxide. The reaction mixture was cooled in an ice bath. After

(56) A. C. Cope, H. L. Bryden, Jr., and C. F. Howell, *Org. Syn.*, **4**, 816 (1963).

stirring for 2 hr, the mixture was extracted by methylene chloride. The solvent was removed and yielded 1 g of crude product which was then purified by chromatography on alumina.

We obtained 530 mg of pure radical (50% yield), mp 74°, esr spectrum in dilute solution in methylene chloride $a_N = 18$ G. *Anal.* Calcd for C₁₁H₁₈NO₂: C, 67.31; H, 9.24; N, 7.14; O, 16.30. Found: C, 67.34; H, 9.35; N, 7.35. The infrared spectrum shows no band in the absorption region 3250 cm⁻¹ (N-H).

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Spectroscopic Studies of Some Laser Dyes

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Abstract: The chief parameters determining laser action of organic dyes are introduced. Favorable constellations in a chromophore are discussed which are necessary to convert it into a potential laser dye; that is, an auxochromic-group-substituted compound showing only small triplet-triplet (T-T) absorption over its fluorescence region. T-T laser photoselection spectroscopy is shown to be a valuable tool for obtaining polarization data on T-T absorption bands. The S-S absorption, fluorescence, and T-T absorption and polarization spectra of *p*-terphenyl, *p*-quaterphenyl, PPO, BBO, POPOP, and α -NPO were measured. T-T absorption and polarization spectra of some of these indicate that an improvement in laser action should occur when they are para-substituted by auxochromes. *p,p'*-Diamino- and *p,p'*-*N,N,N',N'*-tetraethyldiaminoterphenyl, *p,p'*-diamino- and *p,p'*-*N,N,N',N'*-tetraethyldiaminoquaterphenyl, and *p,p'*-dibutoxy-POPOP were synthesized. Their T-T absorption showed remarkably large red shifts; moreover, the bands for the aminooligophenylenes were very broad. This indicates nonplanarity of higher triplet states. Out-of-plane molecular electronic states reduce quantum fluorescence yield. To improve laser performance, ways to render the molecule coplanar are presented. Commercially available laser dyes are classified according to their constellations, and some of their spectroscopic data are presented. It is concluded that dyes with far better laser action properties could be synthesized. Some suggestions are made as to which chromophores appear most promising for conversion into potential laser dyes.

Organic compounds (laser dyes) showing laser action under flashlamp excitation can be divided into two classes.

A. Compounds belonging to the classical organic dyes, like rhodamine 6G, fluorescein, seven-position substituted coumarin, and others^{2a} make up the first class. In these molecules, benzene rings (or its heterocyclic derivatives) are positioned adjacent to each other, as in naphthalene, anthracene, acridine, etc. According to dyestuff theory, an organic dye is formed by the substitution of a hydrogen atom(s) in a chromophore (parent aromatic compound) by a so-called auxochromic group(s) like R₂N, RHN, H₂N, HO, and RO. The fluorescence region (laser action region) of these compounds stretches from the violet to the near-infrared region. Chromophores have in general rather low (or sometimes zero) quantum fluorescence yield ϕ_F . Many of the classical dyes have a ϕ_F close to unity.

(1) (a) Naval Electronics Laboratory Center; (b) Naval Weapons Center.

(2) (a) J. T. Warden and L. Gough, *Appl. Phys. Lett.*, **19**, 345 (1971). This paper gives a summary of flashlamp pumped laser dyes reported in the literature up to July 1971; (b) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1971.

B. Laser action under flashlamp excitation has also been reported in the so-called organic scintillators.^{2a} Remarkably, these compounds are not organic dyes in the classical sense, since they contain no auxochromic groups. The spectral region of these compounds extends from the near ultraviolet (*p*-terphenyl at about 3400 Å) to the blue. Although containing no auxochromic groups, many of the organic scintillators have a ϕ_F close to unity.^{2b}

Organic scintillators, for reasons which will become apparent later, should actually be subdivided into two subgroups. (a) The first is chain-type molecules. They are either phenyl rings joined together by single carbon-carbon bonds (*e.g.*, *p*-terphenyl) or five-membered rings like oxazole, joined to phenyl rings, like POPOP (2,2'-*p*-phenylenebis(5-phenyloxazole)), BBO (2,5-di(4-biphenyl)oxazole), and others.^{2a} (b) The second is combinations of groups belonging to class B with chromophores belonging to class A, like α -NPO (2-(1-naphthyl)-5-phenyloxazole).^{2a}

One can to some extent predict the amount of T-T absorption present over the fluorescence region of an organic dye from the polarization characteristics of its lowest energy S-S absorption band(s) and T-T absorption band(s) located in or near the fluorescence