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Registry No.—**3a,** 61558-34-7; **3b,** 61616-95-3; **4a,** 39762-82-8; **4b,** 39762-83-9; **5a,** 41158-22-9; **5b,** 41158-23-0; **6a,** 41158-15-0; **6b,** 41158-16-1; **7a,** 52265-58-4; **7b,** 52265-59-5; **8a,** 26339-67-3; **8b,** 26339-68-4; **9a,** 33996-03-1; **9b,** 33996-04-2; **10a,** 41158-21-8; **10b,** 41158-20-7; **14,** 13407-03-9; **15,** 16352-21-9; **16,** 33554-05-1; **17,** 61558-35-8; equatorial methyl phosphite, 7735-82-2; axial methyl phosphate, 7735-86-6; 2-methyl-1,3,2-dioxaphosphorinane, 61558-36-9; methyl iodide, 74-88-4.

Supplementary Material Available. A listing of the dielectric, refractive index, and orientation polarization data (1 page). Ordering information is given on any current masthead page.

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Δ^2-1,2,4-Oxadiazolines. 1. Molecular Orbital Calculations, Absorption, and Fluorescence Spectra

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Molecular orbital calculations of five Δ^2-1,2,4-oxadiazolines and one oxadiazole have been carried out using a CNDO/2 method. The results are in accordance with the experimentally observed values. The calculations strongly support a planar cyclic structure. Striking differences have been observed between the fluorescence spectra of the oxadiazolines and the oxadiazole. An explanation of this behavior is advanced. A facile aromatization of 5-ethyl-3-phenyl-Δ^2-1,2,4-oxadiazoline to 5-ethyl-3-phenyl-1,2,4-oxadiazole is described.

Substituted 1,2,4-oxadiazoles have been found to exhibit various types of biological activity including analgetic, sedative,[2] fungicidal, and insecticidal.[3] Some of them are also anthelmintic when tested against *Nematospiroides dubius.*[4] Δ^2-1,2,4-Oxadiazolines are partially saturated oxadiazoles and comparatively less work has been done on the former. McCowen et al.[4] have tested a few of them for anthelmintic activity although the results were negative. To our knowledge, the molecular orbital calculations and the fluorescence spectra of oxadiazolines have not yet been reported in the literature. We plan to study the following: (a) absorption and fluorescence spectra, (b) the chemistry of the ring, (c) biological activity, and (d) mass spectra. This article deals principally with item a.

We have already prepared six compounds in small quantities. Activity testing will be undertaken as soon as larger quantities are available. This paper deals with the molecular orbital calculations and the absorption and fluorescence spectra of five oxadiazolines, i.e., 5-ethyl-3-phenyl-Δ^2-1,2,4-oxadiazoline (Ia), 5-ethyl-3-(*p*-tolyl)-Δ^2-1,2,4-oxadiazoline (Ib), 3-(*p*-anisyl)-5-ethyl-Δ^2-1,2,4-oxadiazoline (Ic), 3-(*p*-chlorophenyl)-5-ethyl-Δ^2-1,2,4-oxadiazoline (Id), and 5,5-pentamethylene-3-phenyl-Δ^2-1,2,4-oxadiazoline (III), and one oxadiazole, 5-ethyl-3-phenyl-1,2,4-oxadiazole (II). (See Figure 1.) In addition, an easy formation of II from Ia is discussed.

Experimental Section

The solvents used for spectroscopy were chloroform (Merck, Uvasol) and 2-propanol (Aldrich, spectrograde). Neither had detectable fluorescence upon excitation at the wavelengths used.

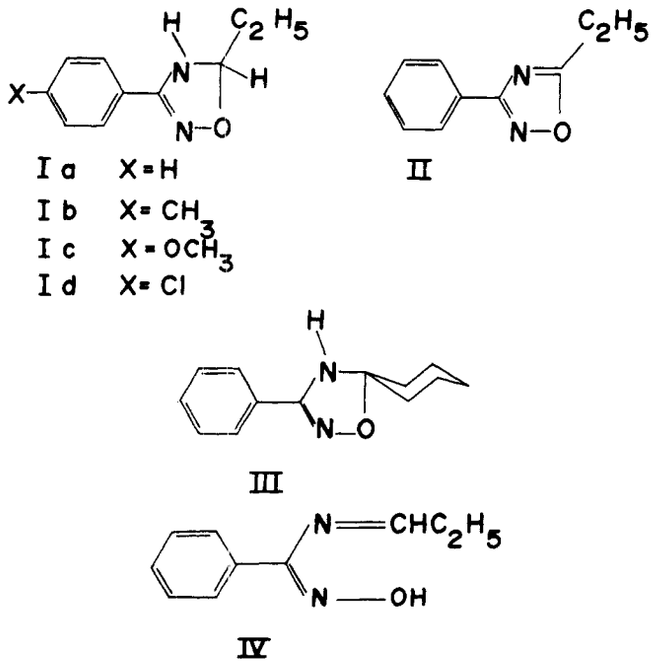

Figure 1. Structures of the molecules treated in this study. (I) 5-ethyl-3-(*p*-X-phenyl)-Δ^2-1,2,4-oxadiazoline, (II) 5-ethyl-3-phenyl-1,2,4-oxadiazole, (III) 5,5-pentamethylene-3-phenyl-Δ^2-1,2,4-oxadiazoline, and (IV) *N*-ethylidenebenzamidoxime (possible open structure of $C_{10}H_{12}N_2O$).

Infrared spectra were obtained on a Perkin-Elmer Model 337 spectrometer. A Varian A-60 and a Varian XL-100 spectrometer have been employed for the nuclear magnetic resonance spectra. Tetramethylsilane was used as internal reference. The fluorescence spectra were taken on an Aminco-Bowman spectrophotofluorimeter (employing a 1P21 photomultiplier) attached to a Hewlett-Packard 7005 B X-Y recorder. All fluorescence spectra were corrected by the method[5] of Chen. The absorption spectra were measured on a Jena Specord spectrophotometer.

Melting points are uncorrected. For thin layer chromatography, silica gel G (Type 60, Merck) has been employed. Benzene–chloroform (1:1) or chloroform was used as developer and iodine vapor for the detection of the spots.

Amidoximes. The amidoximes were prepared as described[6] previously.

5-Ethyl-3-phenyl-Δ^2-1,2,4-oxadiazoline (Ia). This was prepared by the known method.[7] The material obtained was chromatographed over silica gel to remove the starting amidoxime.

The 100-MHz NMR spectrum showed signals at δ 1.00 (3 H, t, CH_3), 1.6–1.96 (2 H, m, CH_2), 5.38 (1 H, b, NH), 5.64 (1 H, q, $J \approx 5$ and 4 Hz), and 7.20–7.76 (5 H, m, Ar).

5-Ethyl-3-(*p*-tolyl)-Δ^2-1,2,4-oxadiazoline (Ib). *p*-Tolylamidoxime (3.64 g, 0.024 mol) dissolved in 800 mL of ethanol–water (1:7) was added to freshly distilled propionaldehyde (1.55 g, 0.027 mol) and allowed to stand at room temperature in a stoppered flask for 16 days. The reaction was followed by thin layer chromatography. Some starting material remained unreacted. At this point the solution was transferred to a separatory funnel, extracted with ether (3 × 75 mL), dried over sodium sulfate, and filtered and the solvent was removed.

The total material, after chromatography over 30 g of silica gel using benzene–chloroform (1:1) as eluent, afforded various fractions containing pure oxadiazoline. Removal of the solvent gave 4 g of crystalline solid, mp 90 °C. Recrystallization from ethanol yielded 3.65 g (79%) of pure crystals, which melted at 95 °C.

The compound was dried at 60 °C for 4 h under vacuum.

Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.47; H, 7.42; N, 14.72. Found: C, 69.40; H, 7.41; N, 14.70.

The NMR spectrum (CCl_4) consisted of signals at δ 2.35 (3 H, s) 5.5 (1 H, q, CH), 5.20 (1 H, b, NH), and 7.27 (4 H, AB q, $J \approx 8.0$ Hz, Ar).

3-(*p*-Anisyl)-5-ethyl-Δ^2-1,2,4-oxadiazoline (Ic). *p*-Anisylamidoxime (1 g, 0.006 mol) was dissolved in 350 mL of water and propionaldehyde (0.38 g, 0.007 mol) was added. The solution was then kept at room temperature for 25 days. Workup followed by chromatography as described for Ib afforded the pure material. Recrystallization from chloroform–hexane provided 0.8 g (64.5%) of crystals, mp 102–103 °C.

Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.06; H, 6.83; N, 13.55.

The NMR spectrum ($CDCl_3$) had peaks at δ 3.85 (3 H, s, OCH_3), 5.05 (1 H, b, NH), 5.70 (1 H, q), and 7.32 (4 H, AB pattern, $J \approx 9$ Hz, Ar). When the spectrum was run in a mixture of CCl_4 and CH_3OD a triplet appeared for the C_5 proton at δ 5.70.

3-(*p*-Chlorophenyl)-5-ethyl-Δ^2-1,2,4-oxadiazoline (Id). Id was prepared as described above and after purification 48% of the crystalline compound with mp 105 °C was obtained.

Anal. Calcd for $C_{10}H_{11}N_2OCl$: C, 57.03; H, 5.23; N, 13.30. Found: C, 57.02; H, 5.25; N, 13.30.

The NMR spectrum ($CDCl_3$) showed signals at δ 4.97 (1 H, b, NH), 5.62 (1 H, q, CH), and 7.4 (4 H, AB q, $J \approx 9.0$ Hz, Ar).

5-Ethyl-3-phenyl-1,2,4-oxadiazole (II). To Ia (0.4 g, 0.002 mol) in 50 mL of benzene was added *N*-bromosuccinimide (0.4 g, 0.002 mol) and a few crystals of azobisisobutyronitrile. The mixture was refluxed for 30 min and cooled. Washing of the benzene layer with 5% aqueous sodium carbonate solution, drying over sodium sulfate, filtration, and solvent removal gave a liquid weighing 0.35 g. Distillation provided a colorless liquid. Owing to the limited quantity obtained, the boiling point could not be determined.

The infrared spectrum was consistent with the structure assignment. The NMR spectrum ($CDCl_3$) showed signals at δ 1.42 (3 H, t, CH_3), 2.97 (2 H, q, $-CH_2-$), 8.22 (2 H, aromatic, ortho), and 7.55 (3 H, aromatic, meta and para).

5,5-Pentamethylene-3-phenyl-Δ^2-1,2,4-oxadiazoline (III). By modification of the previously published method[4] the yield was improved from 25% to 46%. Benzamidoxime (2 g, 0.015 mol), cyclohexanone (1.48 g, 0.015 mol), and 30 mL of glacial acetic acid were heated at 70–90 °C for 5 h. Removal of acetic acid under vacuum, dissolution of the residue in ether, washing the solvent layer with a saturated solution of sodium bicarbonate (aqueous), drying over sodium sulfate, and solvent removal left a solid. On a thin layer chromatogram it showed the presence of starting material and some other impurities. Chromatography over 15 g of silica gel followed by elution with chloroform gave 1.45 g (46%) of chromatographically pure and crystalline substance, which upon recrystallization from ethanol provided the compound which melted at 160 °C (reported[4] 160–161 °C).

The NMR spectrum ($CDCl_3$) showed signals at δ 1.33–2.30 (10 H, m, CH_2), 4.66 (1 H, b), and 7.3–8.08 (5 H, m, Ar).

Table I. Molecular Orbital Calculation Results

	μ_{Gd}, D	μ_{S^*}, D	E_{S^*}, eV	f
Ia[a]	4.90	8.98	7.36	0.26
Ib[a]	5.09	8.46	7.33	0.31
Ic[a]	4.97	9.02	7.32	0.32
Id[a]	4.33	9.47	7.26	0.33
II[a]	1.55	2.32	7.35	0.00
III[b]	4.88	8.87	7.44	0.27
IV[c]	1.02	10.37	2.13	0.00
V[d]	3.69	9.41	4.23	0.00

[a] A methyl group is substituted in the 5 position in place of the ethyl group. [b] Two methyl groups are substituted for the pentamethylene group. [c] Corresponding open-chain; *N*-ethylidenebenzamidoxime. [d] Nonplanar heterocyclic structure with oxygen out of plane.

Methods

Description of the Molecular Orbital Calculations. The calculations are a modified CNDO/2 type with the excited singlet states being calculated by taking the solution of the ground state as the basis set, constructing 64 singly excited configurations, being all of the possibilities $N-7, \ldots, N \rightarrow N+1, \ldots, N+8$ (N being the HOMO), and diagonalizing the configuration interaction matrix.[8]

The modifications in the original CNDO/2 formulation are the following: (1) Instead of using the Slater orbital exponents (ξ) a set of "best" exponents was used which was obtained from the reported[9] results on a series of small molecules by

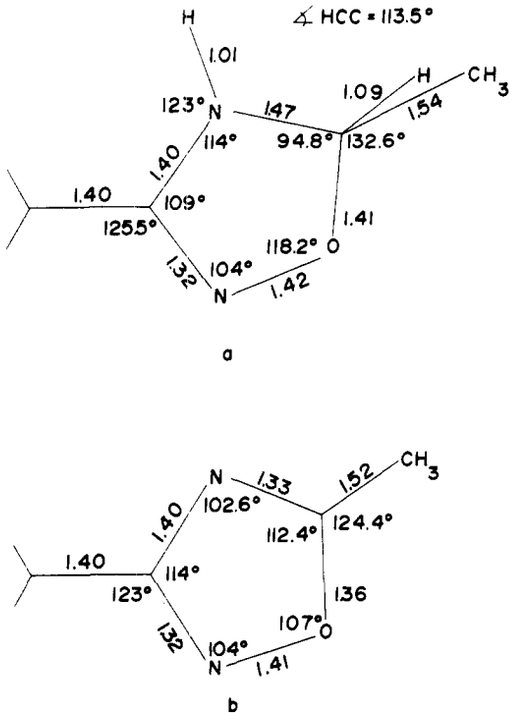

Figure 2. Assumed geometries of the heterocyclic ring in the molecular orbital treatment of (a) the Δ^2-1,2,4-oxadiazolines (angles shown at position 5 between ring atoms and the hydrogen and methyl substituents are with respect to the latters' projection in the plane of the ring; the C–CH_3 and C–H bonds at position 5 make the same angle with the plane of the ring) and (b) 1,2,4-oxadiazole.

means of INDO.[10] (2) Cl was taken to be a pseudo-second-row atom, following the suggestion of Kollman et al.,[11a] and their value of ξ was retained. The α and β values used were from Deb and Coulson.[11b] (3) The overlap integrals were calculated using the summations of Silver and Ruedenberg.[12] (4) The criterion for convergence was taken by comparison of the differences in the bond order matrix[13] between consecutive diagonalizations. Convergence was considered to obtain when (a) not a single element within the bond order matrix changed as much as 0.01, and (b) the sum of the absolute differences was not greater than $0.001J$ (J being the number of orbitals).

Standard geometry[14] was assumed, with the exceptions of the oxadiazole and oxadiazoline rings. These, because of angle strain in 5-membered rings, could only be constructed to satisfy the Pople–Gordon geometry if the ring was taken as nonplanar. Calculations on oxadiazoline showed a totally planar ring to be more stable than one with the oxygen out of the plane (structure V, Table I) by some 4 eV. (In addition, the latter is predicted to have an extremely weak first transition, contrary to what is observed experimentally.) Therefore, a planar structure was chosen. (See Figure 2.) An open structure for oxadiazoline was also considered. (See Discussion.) The calculations were made substituting a methyl group for the ethyl group and two methyl groups for the pentamethylene substituent. This involved a saving in computation time and memory space. Preliminary calculations showed the wave function to be basically unchanged. II was also taken as totally planar. The geometry assumed is shown in Figure 2.

Results

Synthesis. Condensation of benzonitrile or substituted benzonitrile with hydroxylamine hydrochloride in alcoholic solution containing sodium carbonate provided the corresponding amidoximes in 32–70% yield. The amidoximes, when

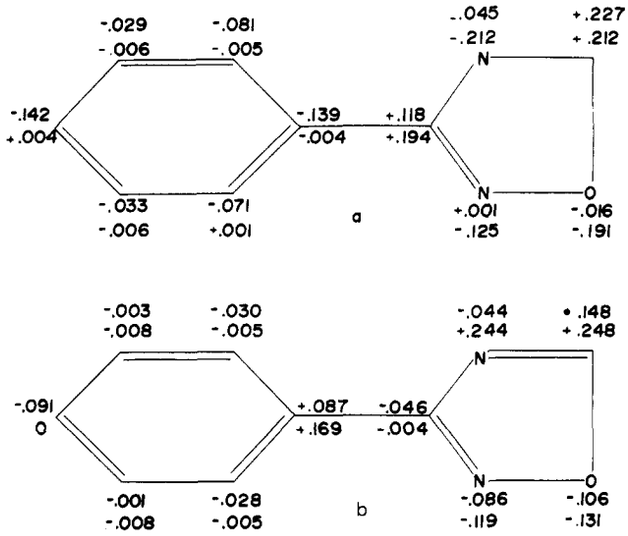

Figure 3. Calculated charges on ring atoms (electronic units). First excited singlet shown above ground state: (a) 5-methyl-3-phenyl-Δ^2-1,2,4-oxadiazoline, and (b) 5-methyl-3-phenyl-1,2,4-oxadiazole.

Table II. Experimental Spectroscopic Results

	Chloroform (ϵ 4.8)		2-Propanol (ϵ 18.3)		
	λ_{abs}, nm	λ_{Fl}, nm	λ_{abs}, nm	λ_{Fl}, nm	f_{CHCl_3}
Ia	285	415	292	439	0.18
Ib	283	407	289	433	0.25
Ic	283	427	285	437	0.46
Id	291	436	301	449	0.37
II	284	310	284	304	0.00
III	291	410	297	414	0.13

allowed to react with propionaldehyde, provided the desired oxadiazolines, Ia–d. Three of these, Ib–d, have not been reported previously. Compound Ia, when allowed to react with *N*-bromosuccinimide in the presence of a catalytic amount of azobisisobutyronitrile, readily afforded II.

Molecular Orbital Calculations. Perhaps the most striking feature of the calculated results (Table I) is the large dipole moment (approximately 5 D) of all of the oxadiazolines in the ground state, whereas the oxadiazole dipole moment (1.6 D) is considerably smaller. Supporting experimental evidence is found in the qualitative observation that Ia–d are not perceptibly soluble in *n*-hexane, whereas II is. We also note that the excited singlet dipole moments for Ia–d increase dramatically (to approximately 9 D) whereas the increase in the dipole moment of II upon excitation is considerably smaller. (See Figure 3.) In considering the calculated energies of excitation we note that they are basically constant for all I and II. The calculated oscillator strengths are reasonably close to the experimental ones, correctly predicting the first excited singlet of II to be an n–π^* state.

Absorption and Fluorescence Spectra. The experimental spectroscopic results are shown in Table II. We point out five salient factors in these results. The first is that the absorption peak for the first excited state is basically the same for Ia and II, whereas the fluorescence peak of Ia is far to the red of that of II. Because the Ia fluorescence peak is also far to the red of what might be expected from a double ring planar system (in comparison, diphenyl in solution shows[15] a doublet fluorescence band which centers at approximately 310 nm), excimer formation appeared to be a very real possibility. However, no concentration dependence was found in the fluorescence spectra. In addition, the wavelength of the maximum at liquid air temperature is not radically different

from that at room temperature. Excimer formation was thus ruled out.

The second point is that although the p-Cl substituent causes a shift to longer wavelength, both p-CH_3 and p-CH_3O shift the absorption and fluorescence to shorter wavelength. This is in apparent contradiction to the general rule that any substituent (by increasing the size of the molecule) will cause a red shift according to the free electron theory. Thirdly, we point out that an electron-donating substituent on the phenyl ring (CH_3O and CH_3) has the opposite effect on absorption as that of an electron-donating substituent on the oxadiazoline ring, pentamethylene. Fourth, pentamethylene red shifts absorption but blue shifts fluorescence. Finally, we indicate that the shifts due to increasing the polarity of the solvent are to the red for the oxadiazolines, but blue for the oxadiazole.

Discussion

Synthesis and Structure. Δ^2-1,2,4-Oxadiazolines have been known for a long time. Previous workers simply assumed a cyclic structure without explanation, although there exists the possibility of an open structure (Figure 1). A recent infrared study found[16] that the NH stretching frequency generally occurred around 3400 cm^{-1}, supporting the cyclic structure. Our molecular orbital calculations on both 5-methyl-3-phenyl-Δ^2-1,2,4-oxadiazoline and N-ethylidenebenzamidoxime indicate the former to be more stable by some 10 eV. In addition, the calculations predict the first excited singlet state for the open structure to be due to an n–π^* transition, plainly in conflict with experiment. (See Table I.) The mass spectra results[17] also support this structure.

In the 100-MHz NMR spectrum the methine proton (H-5) appeared at δ 5.64 as a quartet. When the methyl protons were irradiated, there was no change on H-5, indicating the absence of any long-range coupling. Irradiation of the methylene protons at δ 1.76 collapsed the H-5 signal to a doublet with $J \approx 4.0$ Hz. In this double resonance spectrum the 5.0-Hz coupling was lost. This J value between H-5 and methylene protons was verified by deuterium exchange, wherein CH appeared as a triplet with $J \approx 5.0$ Hz. The double resonance experiment confirms the existence of a cyclic structure and rules out the open-chain form, IV.

Regarding the mechanism of the formation of II, presumably 4-bromo-5-ethyl-3-phenyl-Δ^2-1,2,4-oxadiazoline was an intermediate followed by the quick elimination of hydrogen bromide to give II. The possibility of another intermediate, 5-bromo-5-ethyl-3-phenyl-Δ^2-1,2,4-oxadiazoline, cannot be eliminated. It was not possible to isolate any of these intermediates under the experimental conditions because HBr elimination was quite fast. In any event, either of the intermediates would lose HBr to provide oxadiazole. Compound II has previously been prepared[18] by another method.

Absorption and Fluorescence Spectra. The experimental spectroscopic results can be explained on the basis of the following model: (1) the oxadiazoline ring is planar and in the same plane as the phenyl ring; (2) the ground state of Ia–d has a high dipole moment, the phenyl ring donating electrons to the heterocyclic ring; (3) II is also totally planar, however the ground state dipole moment is much lower; (4) the dipole moment of the first excited state of Ia–d is considerably larger than in the ground state, but with the heterocyclic ring donating electrons to the phenyl ring; (5) the first excited singlet state of II is only slightly more polar than its ground state, and the oxadiazole ring is negative in both cases.

Therefore we attribute the general blue shift of electron-donating groups (CH_3 and CH_3O) on the phenyl ring to stabilization of the ground state and destabilization of the excited state. The large fluorescence red shifting of Ia–d with respect to II we attribute to solvent stabilization of the former owing to the much larger excited state dipole moment of the former [$\Delta G_{solv} = \Delta G(\mu^2)$]. The effect of the pentamethylene substituent is to red shift absorption by means of stabilization of the excited state and destabilization of the ground state. However, the blue shifted fluorescence we explain on the basis of less solvation stabilization in the excited state owing to a smaller excited state dipole moment in III than Ia. All of these explanations are consistent with the results presented in Table I; however, the last does exaggerate the calculated differences.

Concluding Remarks. Oxadiazoles and oxadiazolines apparently have very similar structures and were expected to have similar electron distributions. We have calculated strikingly different wave functions in the two cases both in the ground and the first excited singlet state. These calculations are supported by spectroscopic results. We suggest that the biochemical behavior of oxadiazolines will be found to be very different from that of the corresponding oxadiazoles.

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Registry No.—Ia, 37467-27-9; Ib, 61477-41-6; Ic, 61477-42-7; Id, 61477-43-8; II, 10364-68-8; III, 16013-20-0; propionaldehyde, 123-38-6; p-tolylamidoxime, 19227-13-5; p-anisylamidoxime, 5373-87-5; p-chlorophenylamidoxime, 5033-28-3; benzene, 71-43-2; benzamidoxime, 613-92-3; cyclohexanone, 108-94-1.

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