Substituted Diazacyclopentadienone Anion Radicals

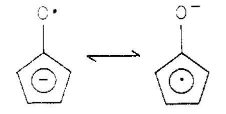
Gerald R. Stevenson,*[1] John F. Hansen,*[1] Gary Clark,[1] and Jeremiah P. Freeman[2]

Departments of Chemistry, Illinois State University, Normal, Illinois 61761, and the University of Notre Dame, Notre Dame, Indiana 46556

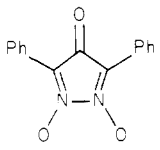
Received March 22, 1979

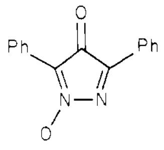
A series of substituted 3,4-diazacyclopentadienone *N*,*N*-dioxides and *N*-oxides were synthesized and their anion radicals were generated via low-temperature potassium metal reduction in tetrahydrofuran. The ESR coupling constants in conjunction with INDO spin density calculations indicate that the spin and charge densities are nearly equally distributed between the ring system and the carbonyl oxygen. The stability of the anion radicals is attributed to the formation of tight ion pairs with the potassium cation. This tight ion association splits the degeneracy of the four nitrogens in the anion radical of 2,2′,5,5′-tetraphenyl-3,3′,4,4′-tetraazafulvalene 3,3′,4,4′-tetraoxide. The anion radical of 2,5-diphenyl-3,4-diazacyclopentadienone *N*,*N*-dioxide loses an oxygen atom upon warming, leaving the anion radical of the corresponding *N*-oxide.

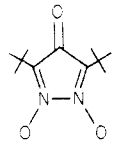
Because of its interesting relationship with Hückel's 4*n* + 2 rule, cyclopentadienone has been the subject of numerous reports.[3] Unlike tropone, which exhibits a diamagnetic ring current, shows a large dipole moment with an electropositive ring system, and forms an anion radical in which the odd electron resides predominately in the seven-membered ring system,[4-6] cyclopentadienone would be expected either to show a "reverse" polarity or to be antiaromatic in character. Further, the odd electron in the anion radical of cyclopentadienone is distributed as shown in the structures I and II. Structure II can be viewed as the anion radical resulting from the reduction of neutral cyclopentadienone showing antiaromatic character. The questions concerning the neutral cyclopentadienone remain for the most part unanswered due to the kinetic instability of cyclopentadienone[7] and difficulty in interpreting the chemical shifts of the relatively stable 2,4-di-*tert*-butylcyclopentadienone.[8,9] However, the recent ESR spectrum observed for the cyclopentadienone ketyl seems to confirm the fact that it is a resonance hybrid of structures I and II.[10]

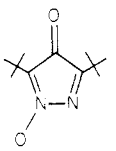

I II

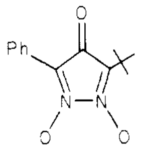
Almost ten years ago Freeman and co-workers[11] synthesized a series of substituted 3,4-diazacyclopentadienone *N*-oxides and *N*,*N*′-dioxides. Since these compounds are kinetically stable heterocyclic analogues of cyclopentadienone and they would form anion radicals of theoretical interest, we were prompted to synthesize several new diazacyclopentadienones (C–F) and investigate the electron distribution in their anion radicals.

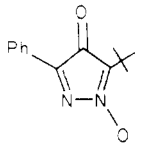

A


B


C


D

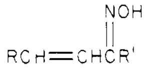

E

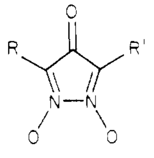

F

At the time of the initial synthesis of the diazacyclopentadienone *N*,*N*-dioxides and *N*-oxides the theoretical significance of the electron distribution in the anion radicals was recognized, and electrochemical reductions of A and B were carried out at room temperature.[11] Identical ESR spectra were obtained for both species. This ESR spectrum was reported to be very complex with apparent unequal coupling to both nitrogens, and it was impossible to relate the ESR spectrum to the structure of the anion radical. It is our intention here to resolve the problem of the two reductions yielding the same anion radical and to assign the coupling constants for the parent anion radicals of compounds A–F.

Results and Discussion

Synthesis. The 3,4-diazacyclopentadienone 3,4-dioxides included in this study were prepared by nitrosation of the unsaturated oximes (N). The synthesis of A by this method has been reported,[11] and the remaining compounds were prepared in a like manner. Spectral data (IR, UV, ^{1}H NMR, and mass spectra) were fully consistent with the assigned structures, and satisfactory analyses (C, H, and N) were obtained for C and E.


N


A, R = R′ = C_6H_5
C, R = R′ = *t*-Bu
E, R = C_6H_5; R′ = *t*-Bu
E-d_5, R = C_6D_5; R′ = *t*-Bu
A-d_{10}, R = R′ = C_6D_5

The dioxides were reduced with sodium dithionite to the 1,4-dihydroxypyrazoles (P), which were oxidized with Fremy's salt (potassium nitrosodisulfonate) to the 3,4-diazacyclopentadienone 3-oxides. This procedure has been used previously for the conversion of A to B,[11] and the other compounds in this series were obtained in the same

---

[1] Illinois State University, where correspondence should be sent.

[2] University of Notre Dame.

[3] (a) K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974); (b) T. Koenig, M. Smith, and W. Snell, *J. Am. Chem. Soc.*, **99**, 6663 1977, and references cited therein.

[4] P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971, p 104.

[5] P. Furderer and F. Gerson, *J. Phys. Chem.*, **82**, 1175 (1978).

[6] Y. Ikegami and S. Seto, *Bull Chem. Soc. Jpn.*, **41**, 2225 (1968).

[7] C. H. DePuy and C. E. Lyons, *J. Am. Chem. Soc.*, **82**, 631 (1960).

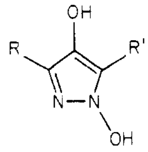
[8] E. W. Garbisch and R. F. Sprecher, *J. Am. Chem. Soc.*, **91**, 6785 (1969).

[9] P. J. Garratt, ref 4, p 105.

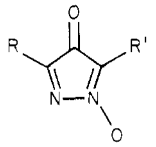
[10] G. A. Russell, T. Takano, and Y. Kosugi, *J. Am. Chem. Soc.*, **101**, 1491 (1979).

[11] J. P. Freeman, J. J. Gannon, and D. L. Surbey, *J. Org. Chem.*, **34**, 187 (1969).

0022-3263/79/1944-3211$01.00/0



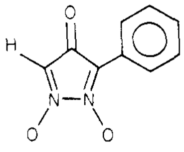
P



B, $R = R' = C_6H_5$
D, $R = R' = t\text{-Bu}$
F, $R = C_6H_5$; $R' = t\text{-Bu}$
F-d_5, $R = C_6D_5$; $R' = t\text{-Bu}$
B-d_{10}, $R = R' = C_6D_5$

way. Again, the spectral properties were in complete agreement with the structural assignments, and satisfactory elemental analyses were obtained for D and F. The selectivity of the reduction of E was clear from the ^{1}H NMR spectrum of P ($R = C_6H_5$; $R' = t$-Bu), which gave a single sharp signal at δ 1.31 for the *tert*-butyl group, with no additional signal for the presence of the isomeric P ($R = t$-Bu; $R' = C_6H_5$).[12] The selectivity of the reduction step was also evident from the mass spectrum of F. Compounds of this type have been shown to have a highly characteristic fragmentation pattern,[13] and the appearance of a major ion of *m/e* 99 (*t*-BuCNO) and the absence of a fragment of *m/e* 119 (C_6H_5CNO) are uniquely consistent with the structure shown for F. The observed selectivity is in accord with earlier reports of the reduction of 3,4-diazacyclopentadienone 3,4-dioxides[11] and 1-hydroxypyrazole 2-oxides.[14]

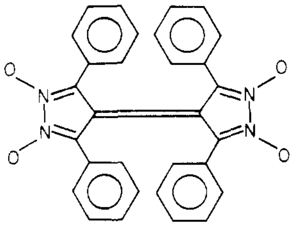
Attempts were made to prepare the compound R using



R

the methods described above. However, nitrosation of either cinnamaldoxime (N, $R = C_6H_5$; $R' = H$) or acrylophenone oxime (N, $R = H$; $R' = C_6H_5$) failed to give the desired product.

The tetraazafulvalene T was prepared by the method described in a previous report.[15]



T

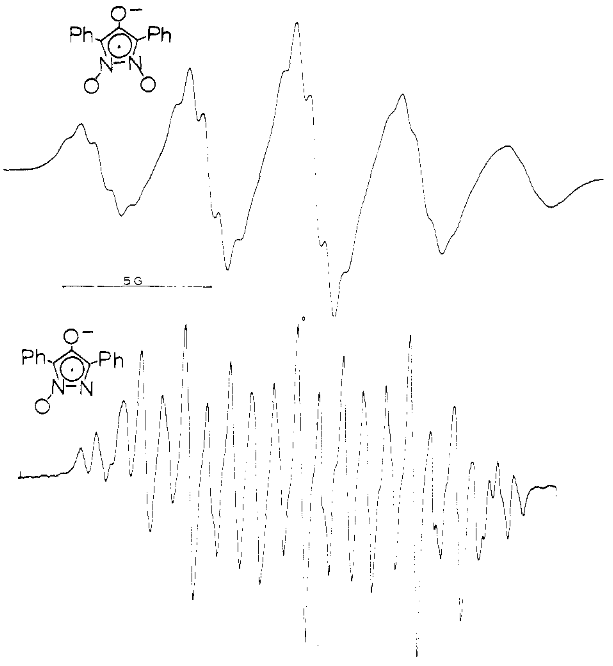


Figure 1. ESR spectra of A$^-\cdot$ (upper) and B$^-\cdot$ (lower) recorded at −50 °C. The lower spectrum can be generated either via the reduction of B or by warming A$^-\cdot$ and recooling the anion radical solution.

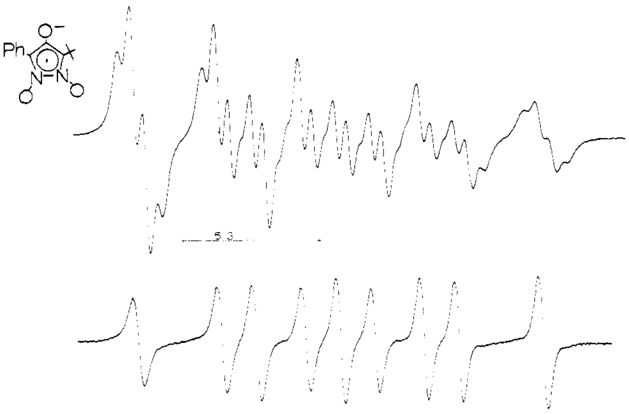


Figure 2. ESR spectra of E$^-\cdot$ (upper) and E-$d_5^-\cdot$ (lower) at −50 °C.

Electron Spin Resonance. The low-temperature reduction of diphenyldiazacyclopentadienone *N,N*-dioxide (A) in tetrahydrofuran (THF) with potassium metal leads to the formation of an anion radical solution yielding a simple but poorly resolved ESR spectrum (Figure 1). This spectrum results from two equivalent nitrogens and six equivalent hydrogens with hyperfine coupling constants of 3.52 and 0.45 G, respectively. This spectrum, however, is not the same as that observed previously for the electrolytic reduction of A by Freeman and co-workers.[11] The hyperfine splittings do not show any temperature dependence from −45 to −125 °C. But, if the anion radical solution is allowed to warm to room temperature and is again placed back into the cooled ESR cavity, an entirely different spectrum is obtained (Figure 1). This spectrum is identical with that observed previously from the electrolytic reduction, and is sufficiently complex to make the ESR spectral interpretation difficult. To shed further light upon the nature of this thermally altered anion radical, A-d_{10} was reduced under the same conditions. This anion radical (A-$d_{10}^-\cdot$) yields a five-line pattern resulting from two equivalent nitrogens with a coupling constant of 3.52 G. The expected deuterium splittings of 0.45/6.5 G are much smaller than the line width and are not observed (Figure 2). After warming, this five-line pattern changes to a nine-line spectrum, which is clearly due to two nonequivalent nitrogens with splitting constants of 3.71 and 1.44 G (Figure 2). From this it is clear that warming

---

(12) The presence of the second isomer would have been easily detected in the ^{1}H NMR, since the spectrum of the analogous compound where $R = R' = t$-Bu shows nicely separated signals for the *tert*-butyl groups at 1.47 and 1.34 ppm, assigned tentatively as the C-3 and C-5 substituents, respectively.

(13) J. F. Hansen and M. J. O'Hare, *J. Heterocycl. Chem.*, 13, 985 (1976).

(14) (a) J. P. Freeman and J. J. Gannon, *J. Org. Chem.*, 34, 194 (1969); (b) J. F. Hansen and D. E. Vietti, *ibid.*, 41, 2871 (1976).

(15) J. P. Freeman and J. F. Hansen, *J. Chem. Soc., Chem. Commun.*, 961 (1972).

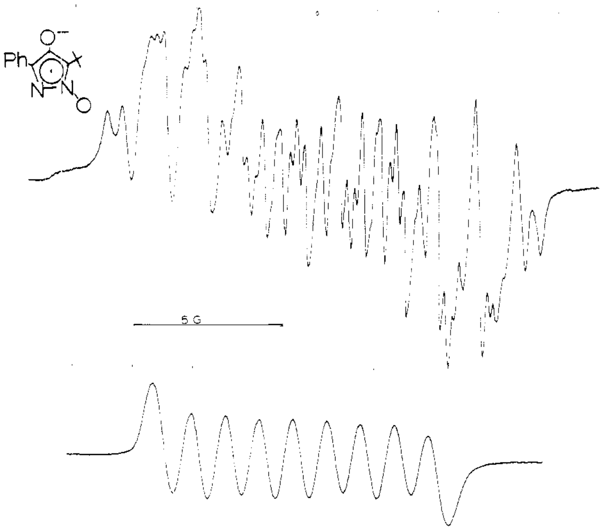


Figure 3. ESR spectra of F$^{-}\cdot$ (upper) and F-$d_5{}^{-}\cdot$ (lower) at −50 °C.

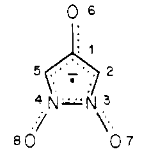
the anion radical solution has split the degeneracy of the two nitrogens.

The reduction of diphenyldiazacyclopentadienone *N*-oxide (B) yields exactly the same spectrum upon ESR analysis as that obtained from warming A$^{-}\cdot$. Further, B-$d_{10}{}^{-}\cdot$ gives the same ESR pattern as does A-$d_{10}{}^{-}\cdot$ after warming. Thus, A$^{-}\cdot$ or A must lose an oxygen atom, resulting in the formation of the anion radical of B. The deuterium studies obviate the hydrogen splitting constants for B-$d_{10}{}^{-}\cdot$, thus allowing easy interpretation of the ESR spectrum of B$^{-}\cdot$. The spectral pattern for this anion radical results from two nitrogens of 3.71 and 1.44 G as well as proton couplings of 1.44 and 0.5 G each from two equivalent protons.

It has been demonstrated that the spin density on the neighboring atoms has only a small effect upon the nitrogen hyperfine coupling constants.[16] This allows the spin densities on the nitrogen p$_z$ orbitals to be taken from $A_N = Q_N\rho_N$. Using a value of 24 G for Q_N,[17] the p$_z$ spin densities (ρ_N) on the two nitrogens are 0.15 for A$^{-}\cdot$ and 0.15 and 0.060 for B$^{-}\cdot$. Apparently the loss of the oxygen atom greatly reduces the spin density on the nitrogen from which it came without significantly altering the other nitrogen spin density. The very small coupling constants for the phenyl ring protons show that the spin density is largely localized in the heterocyclic ring. It is, however, possible that there is a significant spin density on the methine carbons of the phenyl rings.

If indeed the spin density on the methine carbons of the phenyl groups is close to zero, C$^{-}\cdot$ should yield similar nitrogen coupling constants to those of A$^{-}\cdot$. The anion radical of C did yield a narrow five-line pattern resulting from two equivalent nitrogens with a coupling constant of 3.61 G at −50 °C. A_N does not show any thermal dependence down to −100 °C. Warming of the anion radical solution to room temperature results in a loss of the ESR signal, and no evidence for a reaction analogous to that of A$^{-}\cdot$ was observed. The small peaks at the side of each of the major lines (Figure 3) appear at different positions when C is reduced with sodium metal in place of potassium, indicating that they are due to the presence of tight ion pairs. The $m = \pm^1/_2$ lines of the potassium splitting must be buried under the five-line spectrum.

Table I. p$_z$ Spin Densities for the Anion Radicals of C and D Compared to Those Calculated (INDO) for the Anion Radicals of 3,4-Diazacyclopentadienone 3,4-Dioxide and 3-Oxide



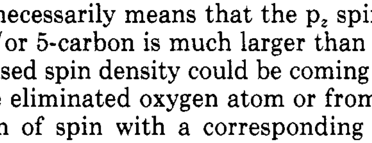
position	dioxide		oxide	
	ρ_{INDO}	ρ_{exptl}	ρ_{INDO}	ρ_{exptl}
1	−0.040	<0.08[a]	−0.053	
2	−0.051	≈0[b]	−0.086	
3	+0.20	0.15	+0.19	0.15
4	+0.20	0.15	+0.081	0.060
5	−0.051	≈0[b]	+0.19	0.2[c]
6	+0.47		+0.55	
7	+0.13		+0.12	
8	+0.13		–	

[a] Calculated from $A_{^{13}C} = 32\rho_1 - 14(\rho_2 + \rho_5)$.[18] [b] Based upon the line widths (lack of unresolved proton splittings). [c] Estimated from the β-proton splittings of 0.1 G.

Although warming of the anion radical of C did not produce D$^{-}\cdot$, the reduction of D did yield this anion radical, which gives an ESR spectrum resulting from two nonequivalent nitrogens of A_N equal to 4.42 and 1.0 G. The hyperfine lines for D$^{-}\cdot$ are obviously broadened by unresolved proton splittings, which can be partially resolved at temperatures below −100 °C. This splitting from the γ protons necessarily means that the p$_z$ spin density on the 2- and/or 5-carbon is much larger than those in C$^{-}\cdot$. This increased spin density could be coming simply from that on the eliminated oxygen atom or from a major redistribution of spin with a corresponding loss of spin density on the carbonyl carbon.

Due to the fact that there are several "blind" spots on the anion radicals, including the carbonyl oxygen and the *N*-oxide oxygens, INDO calculations were carried out on the anion radical of diazacyclopentadienone *N*,*N*-dioxide and *N*-oxide (Table I). From Table I it is clear that the INDO calculated p$_z$ spin densities are in excellent agreement with the experimental spin densities for all of the positions where experimental values could be obtained. This makes it very likely that the INDO calculated values on the oxygen atoms are accurate.

From Table I, the question as to where the increased spin density on the 5-carbon comes from is answered. Upon removal of the 8-oxygen, its spin density is simply relocated upon the p$_z$ orbital of the 5-carbon. Further, the carbonyl oxygen p$_z$ spin density slightly increases as the oxygen atom is removed. All of the data gathered in Table I indicate that the anion radicals discussed here can be described by valence bond structures III and IV.



III IV

The reduction of E yields an anion radical solution that results in a broad poorly resolved ESR signal consisting of two triplets from two different nitrogens of 3.04 and 4.24 G and a quartet due to three equivalent protons (ortho and para) with A_H = 0.37 G. These coupling constants show no thermal dependence from −50 to −80 °C, and further

---

[16] J. H. Freed and G. K. Fraenkel., *J. Chem. Phys.*, **40**, 1815 (1964).

[17] J. E. Wertz and J. R. Bolton, "Electron Spin Resonance Elementary and Practical Applications", McGraw-Hill, New York, N.Y., 1972, p 127.

[18] A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance", Harper and Row, New York, N.Y., 1967, p 94.

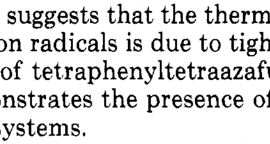
warming of the anion radical solution results only in the loss of the ESR signal. The coupling constants were confirmed via the reduction of the pentadeuterio system, Figure 3 (deuteriums on the phenyl moiety). A reaction analogous to $A^{-}\cdot \rightarrow B^{-}\cdot$ could not be effected for this system. Since the nitrogen coupling constant for $A^{-}\cdot$ is 3.52 G, and that for $C^{-}\cdot$ is 3.61 G, the smaller nitrogen splitting in $E^{-}\cdot$ is considered to be that due to the nitrogen closest to the phenyl group.

Although the thermal transition from $E^{-}\cdot$ to $F^{-}\cdot$ cannot be readily effected at room temperature, the anion radical of F can be generated via potassium metal reduction of F. This anion radical ($F^{-}\cdot$) yields an ESR signal too complex for immediate interpretation, but the interpretation of that due to the phenyl-d_5 system is first order, Figure 3. The anion radical of F yields A_N's of 1.14 and 3.39 G and A_H's of 1.98 for two protons and 0.50 for one proton. These are presumably the ortho and para protons on the phenyl ring. Again, the coupling constants for this anion radical do not exhibit any thermal dependence.

The remarkable lack of temperature dependence of the hyperfine coupling constants for the entire series of anion radicals, the absence of alkali metal coupling, and the excellent agreement between the calculated and experimental spin densities would seem to indicate the lack of ion pairing in these systems. However, it is most likely that these anion radicals are strongly ion paired in THF. The fact that the addition of even small portions of HMPA, which reduces the amount of ion association, results in the immediate polymerization of the anion radical solution suggests that the thermal stability of the monomeric anion radicals is due to tight ion association. The reduction of tetraphenyltetraazafulvalene (T) dramatically demonstrates the presence of tight ion association in these systems.

The potassium reduction of T results in the formation of $T^{-}\cdot$, which yields a simple nine-line ESR pattern that is due to two sets of two equivalent nitrogens with A_N's of 3.40 and 0.31 G.

The nonequivalency of the four nitrogens must be due to the association of the potassium cation with one of the two diazacyclopentadienyl moieties, structure V. This anion radical is stable at room temperature, and the A_N's vary smoothly from 3.50 and 0.68 G at +20 °C to the values given above at −75 °C. The tighter ion association at the higher temperatures results in the larger difference between the nitrogen couplings. The stability of the anion radical is dependent upon the ion association, as the addition of very small amounts of HMPA to the THF solution causes a loss of the ESR signal and the formation of a visible precipitate. The lack of temperature-dependent coupling constants in the single ring systems is evidently due to the fact that the ion pair has a relatively rigid structure analogous to that shown in structure V. For the *N*-oxide systems, the potassium cation is most probably sandwiched between the *N*-oxide oxygen and the unsubstituted nitrogen atom.



V

Experimental Section

2,2,6,6-Tetramethyl-4-hepten-3-one Oxime. A mixture of 3.19 g (19 mmol) of *trans*-2,2,6,6-tetramethyl-4-hepten-3-one,[19] 2.1 g (30 mmol) of hydroxylamine hydrochloride, and 2.0 g (20 mmol) of $BaCO_3$ in 30 mL of 95% ethanol was heated under reflux. After 48 h the mixture was filtered and the hot filtrate was diluted with 15 mL of water and cooled overnight at −20 °C. The white crystalline solid (1.70 g, 49%) was collected and washed with water. The material, mp 88–102 °C, was a mixture of the syn and anti oximes and could be used without further purification. One of the isomers, mp 111–112.5 °C, could be isolated by recrystallization from hexane: ^1H NMR δ 9.3 (br s, 1 H, OH), 6.6 (d, J = 17, 1 H), 5.9 (d, J = 17, 1 H), 1.2 (s, 9 H), and 1.1 (s, 9 H). Anal. Calcd for $C_{11}H_{21}NO$: C, 72.09; H, 11.55; N, 7.64. Found: C, 71.95; H, 11.50; N, 7.70.

3,5-Di-*tert*-butyl-4-oxo-4*H*-pyrazole 1,2-Dioxide. A solution (1.98 g) of the above oxime in 40 mL of 90% acetic acid was stirred under O_2 at 0–5 °C while 1.7 g (25 mmol) of $NaNO_2$ in 10 mL of water was added over 150 min. After an additional 60 min the mixture was diluted with 50 mL of H_2O and extracted with three 25-mL portions of ether. The ether extracts were washed with water, dried (Na_2SO_4), and evaporated. The residue was treated with 10 mL of water and extracted with three 25-mL portions of hexane. The hexane extract was washed with water, dried, concentrated to 20 mL, and applied to a column of 20 g of silica gel (Baker No. 3405). Elution was begun with hexane and fractions were collected when the first colored material appeared. After a forerun of 30 mL of hexane, the product was collected by elution with 150 mL of hexane and then with 50 mL of benzene. These fractions were combined and evaporated, and the product was recrystallized from ethanol–water to give 0.58 g (24%) of yellow needles: mp 76–77 °C; IR 1640 cm^{-1}; ^1H NMR δ 1.40 (s). Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.37; H, 8.02; N, 12.38. Found: C, 58.05; H, 8.00; N, 12.62.

2,5-Di-*tert*-butyl-1,4-dihydroxypyrazole (P; R = R′ = *t*-Bu). A solution of 0.46 g of the compound described above in 10 mL of ethanol (absolute) was added to a solution of 3.0 g of $Na_2S_2O_4$ in 25 mL of water and stirred at room temperature. After 5 h the mixture was diluted with water to 50 mL and cooled overnight. Most of the product was recovered by filtration as a white solid, and extraction of the filtrate with CH_2Cl_2 gave an additional small quantity. The product, 0.36 g (85%), had mp 149–152 °C dec after recrystallization from $CHCl_3$–hexane: ^1H NMR δ 7.50 (br s, OH), 1.47 (s, 9 H, 3-*t*-Bu), and 1.34 (s, 9 H, 5-*t*-Bu). Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.24; H, 9.50; N, 13.19. Found: C, 62.08; H, 9.51; N, 13.03.

3,5-Di-*tert*-butyl-4-oxo-4*H*-pyrazole 1-Oxide (D). A solution of 0.20 g (0.94 mmol) of P in 10 mL of CH_2Cl_2 was treated in a separatory funnel with 0.75 g of potassium nitrosodisulfonate[20] in 15 mL of water. After shaking for 2 min, the organic layer was separated, and the aqueous layer was extracted with two 10-mL portions of CH_2Cl_2. The organic solutions were combined, dried, and evaporated. The residue was sublimed at 60–70 °C (20 torr) to give 0.17 g (85%) of red-orange needles: mp 77–78 °C; IR 1710 and 1565 cm^{-1}; ^1H NMR δ 1.37 (s, *t*-Bu) and 1.38 (s, *t*-Bu). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.78; H, 8.84; N, 13.16.

***trans*-4,4-Dimethyl-1-phenyl-2-penten-1-one Oxime.** A solution of 3.1 g (16 mmol) of *trans*-4,4-dimethyl-1-phenyl-2-penten-1-one,[21] 1.3 g (16 mmol) of NaOAc, and 1.7 g (25 mmol) of hydroxylamine hydrochloride in 30 mL of ethanol–water (2:1) was heated under reflux. After 5 h the solution was diluted with 10 mL of water and cooled overnight at −20 °C to give 1.52 g (46%) of a white solid. Repeated recrystallization from hexane gave a sample, mp 100–103 °C, which was a mixture of the isomeric *E* and *Z* oximes. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.80; H, 8.45; N, 6.89. Found: C, 76.91; H, 8.60; N, 7.10.

5-*tert*-Butyl-3-phenyl-4-oxo-4*H*-pyrazole 1,2-Dioxide. A solution of 1.02 g (5 mmol) of the above oxime in 20 mL of 90% acetic acid was stirred under oxygen at 0–5 °C while 0.8 g (12 mmol) of $NaNO_2$ in 5 mL of water was added over 4 h. After 45 min the mixture was diluted to 50 mL with water and cooled in ice. The supernatant was decanted, and the residual gum was recrystallized from ethanol (95%) to give 0.43 g (35%) of orange needles. After recrystallization from CH_2Cl_2–hexane the material

---

(19) W. Rundel, *Chem. Ber.*, **102**, 374 (1969).

(20) D. J. Cram and R. A. Reeves, *J. Am. Chem. Soc.*, **80**, 3099 (1958).

(21) K. B. Wiberg and B. I. Rowland, *J. Am. Chem. Soc.*, 77, 1159 (1955).

had: mp 107–108 °C; IR 1640 cm^{-1}; ^{1}H NMR δ 8.20 (m, 2), 7.40 (m, 3), 1.38 (s, 9). Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.74; N, 11.37. Found: C, 63.46; H, 5.78; N, 11.29.

5-*tert*-Butyl-3-phenyl-1,4-dihydroxypyrazole. To a solution of 5.0 g (29 mmol) of $Na_2S_2O_4$ in 50 mL of EtOH–H_2O (1:3) was added 0.99 g (4 mmol) of the dioxide described above. After stirring for 3 h at room temperature, the mixture was diluted with water to 50 mL and extracted with three 50-mL portions of CH_2Cl_2. The organic solution was washed with water, dried, and evaporated. The residue gave white prisms from CH_2Cl_2–hexane, mp 90–93 °C dec. The material thus isolated, 0.60 g (55%), was solvated, and it retained 0.5 mol of CH_2Cl_2, even after evacuation overnight at 0.1 torr: ^{1}H NMR δ 8.45 (br s, 2 H, OH), 7.4 (mult, 5, ArH), 5.22 (s, 1, CH_2Cl_2), 1.31 (s, 9, *t*-Bu). Anal. Calcd for $C_{13}H_{16}N_2O_3 \cdot {}^1/_2CH_2Cl_2$: C, 59.02; H, 6.24; N, 10.19. Found: C, 59.08; H, 6.14; N, 10.41.

5-*tert*-Butyl-3-phenyl-4-oxo-4*H*-pyrazole 1-Oxide (F). A solution of 0.35 g (1.3 mmol) of the dihydroxypyrazole from above in 30 mL of CH_2Cl_2 and 2 mL of methanol was shaken in a separatory funnel with 1.5 g of potassium nitrosodisulfonate in 30 mL of H_2O. After 2 min the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated to give 0.22 g (76%) of shiny, red-brown flakes, mp 82–83 °C, after recrystallization from ethanol–water: IR 1715 and 1580 cm^{-1}; ^{1}H NMR δ 8.30 (m, 2), 7.50 (m, 3), 1.40 (s, 9, *t*-Bu). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.16. Found: C, 67.82; H, 6.08; N, 12.00.

3,3′5,5′-Tetraphenyl-1,1′-dihydroxy-4,4′-bipyrazole 2,2′-Dioxide. A solution of 55.8 g (0.25 mol) of chalcone oxime in 200 mL of methanol was stirred under N_2 at 35 °C and treated over 30 min with 58 g (0.5 mol) of isoamyl nitrite. Three times at 2-h intervals portions of solid were filtered off, and the filtrate was treated with additional 29-g portions of isoamyl nitrite. The mixture was allowed to stand overnight, and a final crop of solid was collected. The combined solid was washed with methanol and with ether and was stirred for several hours at room temperature with 500 mL of 10% $NaHCO_3$. The slurry was filtered, and the red-brown solid was washed with water and methanol. The solid, 17.5 g (25%), mp 212–213 °C, was identified as 3,5-diphenyl-4-oximino-4*H*-pyrazole 1,2-dioxide by comparison with an authentic sample.[11]

The aqueous solution was acidified with HCl (concentrated), and the precipitate was collected and washed with water. The moist solid was dissolved with heating in 300 mL of ethanol containing 10 g of KOH. The solution was cooled and diluted to 2000 mL with ether, and the dipotassium salt was collected. Acidification of a cold aqueous ethanol solution of the salt with acetic acid gave the product as a white solid, mp 159–162 °C dec. Anal. Calcd for $C_{30}H_{22}N_4O_4$: C, 71.70; H, 4.41; N, 11.15. Found: C, 71.68; H, 4.46; N, 10.63.

2,2′,5,5′-Tetraphenyl-3,3′,4,4′-tetraazafulvalene 3,3′,4,4′-Tetraoxide (T). A solution of 5.78 g of the dipotassium salt described above in 200 mL of H_2O was stirred at room temperature and treated with 40 mL of 0.25 M I_2–KI solution. After 60 min the mixture was filtered to yield 4.11 g (90%) of green flakes. Recrystallization from CH_2Cl_2–hexane gave shiny green prisms, mp 192 °C dec. An analytical sample was dried at 140 °C (0.5 torr): IR 1580, 1550, 1075 cm^{-1}; UV ($CHCl_3$) 262, 502 nm (log ϵ 4.32, 4.29); mass spectrum 440 (35), 105 (100), 103 (32).

Anal. Calcd for $C_{30}H_{20}N_4O_4$: C, 71.99; H, 4.03; N, 11.20. Found: C, 72.35; H, 4.19; N, 11.33.

The deuterated compounds were prepared in the same manner utilizing the appropriate deuterated starting materials. The isotopic purity of the deuterated compounds was confirmed via ^{1}H NMR and mass spectral analysis.

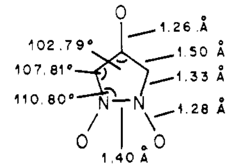
Table II. UV-Vis Spectral Data in Isooctane

compd	λ_{max}, nm	log ϵ	compd	λ_{max}, nm	log ϵ
A	455	3.19	D	395	3.27
	333	3.59		237	3.72
	256	4.58	E	418	3.27
B	508	3.30		285	4.04
	327	3.27		258	4.14
	254	4.24	F	433	3.16
C	372	2.34		319	3.95
	283	3.90	T[a]	502	4.29
				262	4.32

[a] Spectral data for T were taken in $CHCl_3$, as this compound is not sufficiently soluble in isooctane.

X-Band ESR spectra were recorded on a Varian E-4 spectrometer. The temperature was controlled within 3 °C with a Varian V-4557 variable temperature controller, which was calibrated with an iron–constantan thermocouple. UV–visible spectra were run in isooctane using a Beckman Acta VI spectrophotometer.

The INDO program used is available from the Quantum Chemistry Program Exchange.[22] The INDO calculations were carried out using the standard bond lengths for the planar system shown below.



The bond angles and distances were assigned from a comparison of X-ray structure reports for similar compounds. The angles were chosen to maximize the area of the five-sided figure.

The spectral data for the neutral compounds used in this study are summarized in Table II.

Registry No. A, 17952-96-4; B, 17953-08-1; C, 70968-47-7; C anion radical, 70968-48-8; D, 70968-49-9; D anion radical, 70968-50-2; E, 16917-81-0; F, 70968-51-3; (*E*,*E*)-N (R = R′ = *t*-Bu), 70968-52-4; (*Z*,*E*)-N (R = R′ = *t*-Bu), 70968-53-5; (*E*,*E*)-N (R = *t*-Bu; R′ = Ph), 61572-40-5; (*Z*,*E*)-N (R = *t*-Bu; R′ = Ph), 70968-54-6; P (R = R′ = *t*-Bu), 70968-55-7; T, 37422-14-3; *trans*-2,2,6,6-tetramethyl-4-hepten-3-one, 20859-13-6; *trans*-4,4-dimethyl-1-phenyl-2-penten-1-one, 29569-93-5; 3,3′,5,5′-tetraphenyl-1,1′-dihydroxy-4,4′-bipyrazole 2,2′-dioxide, 37422-13-2; 3,3′,5,5′-tetraphenyl-1,1′-dihydroxy-4,4′-bipyrazole 2,2′-dioxide dipotassium salt, 70968-56-8; 3,5-diphenyl-4-oximino-4*H*-pyrazole 1,2-dioxide, 71000-85-6; chalcone oxime, 6502-38-1; 3,4-diazacyclopentadiene 3,4-dioxide anion radical, 70968-57-9; 3,4-diazacyclopentadiene 3-oxide anion radical, 70968-58-0.

Supplementary Material Available: ESR spectra for A-$d_{10}^{-}\cdot$, B-$d_{20}^{-}\cdot$, $C^{-}\cdot$, and $T^{-}\cdot$ (3 pages). Ordering information is given on any current masthead page.

---

[22] P. A. Dobsh, Quantum Chemistry Program Exchange, Vol. 11, Department of Chemistry, Indiana University, Bloomington, Ind., 1969, p 141.