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Use of bis-aryloxalate neat solid samples to investigate ferromagnetic phenoxy-phenoxy geminate geminate coupling is described. The title compounds (described in Technical Report 16) form good crystals, which up cooling to 77K or below and irradiation with a Xenon arc lamp give ESR spectra indicating both monoradical signals and radical-radical triplet pair interactions. The size of the interaction may be qualitatively determined by the spectral extent of the triplet spectrum (80-120 Gauss), which at this preliminary stage suggests that the radicals are 6.0-7.0 angstroms apart. The spectra are shown and compared to spectra with similar features for solid state photolysis of diphenyl oxalate. Tert-butylated bis-aryloxalates show good radical pair stability, with triplet ESR signals surviving days at room temperature in some cases.			
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Technical Report #17

**SOLID STATE PHOTOCHEMICAL GENERATION OF
TRIPLET PHENOXY-PHENOXY RADICAL PAIRS**

by Paul M. Lahti* and David A. Modarelli

Progress Report



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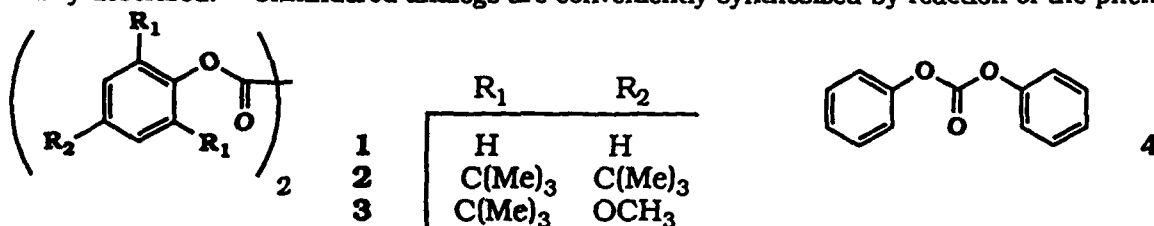
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ABSTRACT: Photochemical irradiation of neat, crystalline samples of *bis*-aryloxalates at 77 K leads to production of strong ESR signals characteristic of both monoradical phenoxy production and of triplet spin-coupled phenoxyl radical pairs. Without 2,6-di-*tert*-butyl stabilization, these signals decay before reaching room temperature, but with steric stabilization the radical pair signals are persistent.

INTRODUCTION: Technical Reports 11, 12, 14, and 16 have described our synthetic development of molecules from which aryloxy radicals may be generated by photochemical or thermal means, in frozen matrix, in polymer matrix, or in the neat solid state.¹⁻⁴ In particular, Technical Report 16⁴ describes our synthesis of *bis*-aryloxalates as convenient, stable photochemical sources of phenoxyl radicals. In this report, we describe the use of single crystal photolysis of such diaryl oxalates to produce -- in addition to the expected monoradicals -- triplet (T) state spin-coupled radical pairs, the detection of the triplet pairs by electron spin resonance (ESR) spectroscopy, and their qualitative stability as a function of temperature.

EXPERIMENTAL METHODS: Synthesis of *bis*-aryloxalates (BAO's) is readily carried out by reaction of the lithium salts of hindered phenols with oxalyl chloride in ether with cooling by an ice bath, as previously described.⁴ Unhindered analogs are conveniently synthesized by reaction of the phenols



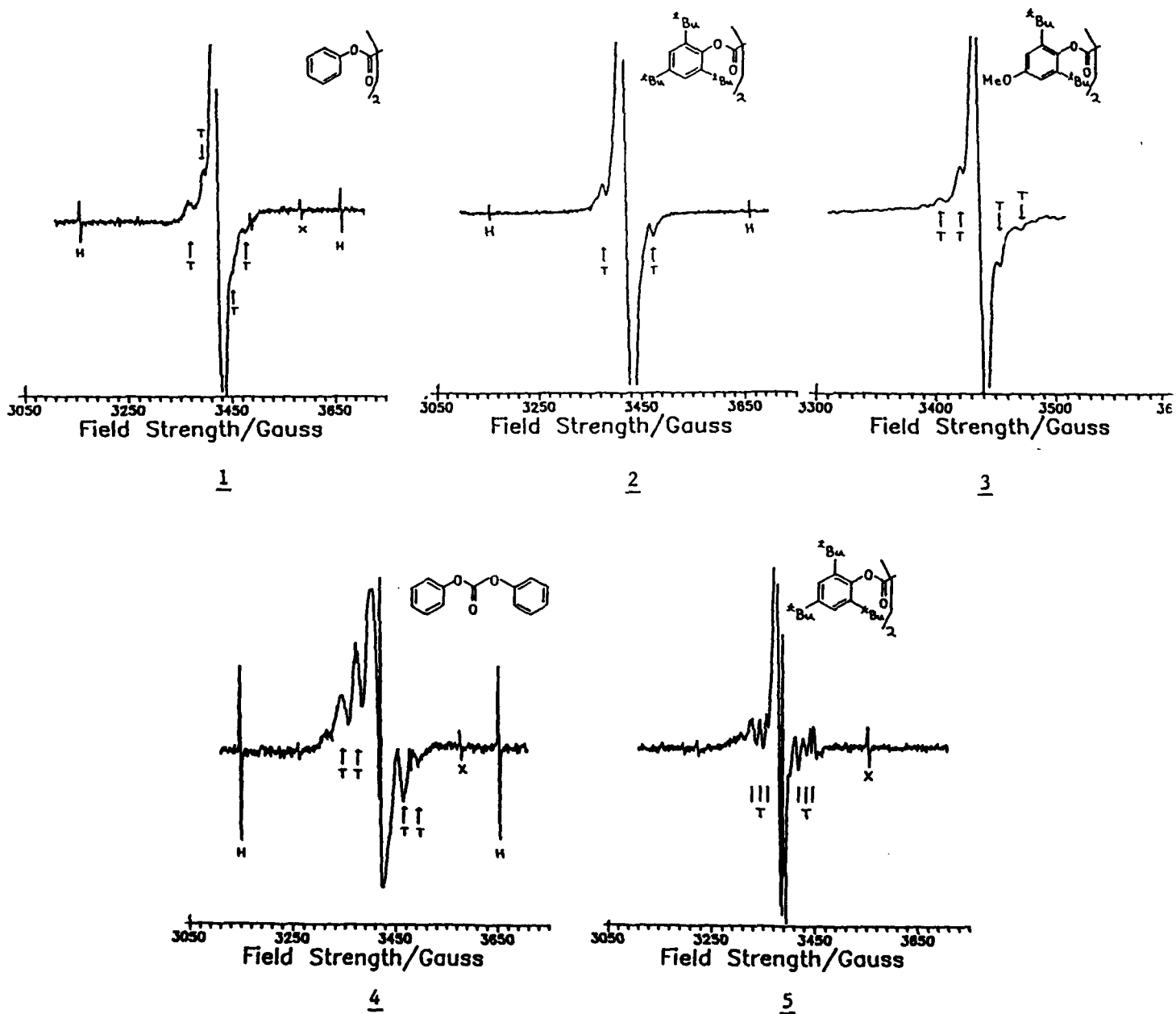
with oxalyl chloride in pyridine. We have synthesized symmetrical BAO's 1-3 shown on the previous page. All new compounds have satisfactory elemental analyses and spectral properties expected for their assigned structures. All are thermally stable at room temperature, and may be stored for long periods in the dark on the benchtop. Slow recrystallization of these compounds from ethanol or ethanol:water mixtures typically leads to formation of long, colorless, needle-shaped crystals, although some effort is required to avoid fast crystallization in a powdery form.

For most samples, a single crystal was carefully placed in a quartz or Suprasil ESR tube and the tube evacuated to less than one mTorr. These samples could be maintained at 77K in a Suprasil ESR dewar purchased from Wilmad Glass Company, Inc. For long-term low temperature work, single crystal samples were affixed by Apiezon N grease to a high-purity copper spindle sample holder that was specially machined to screw into the thermal heat-transfer stage of an APD Cryogenics Displex closed-cycle circulating helium cryostat. The cryostatic unit was mounted on a mobile cart, and attached to a vacuum line capable of evacuating the sample assembly of the Displex to below 0.1 mTorr. The sample spindle was maintained under vacuum by means of a Suprasil outer shroud, and cooled to 12 K by the Displex assembly. A thermal gradient between the base of the cooling stage and the actual sample position is likely; the magnitude of this gradient has not yet been measured, but is unlikely to be greater than 5 K based on similar apparatus.

Photochemical irradiation was carried out upon precooled samples using a Kratos 1000 W Xenon arc with a quartz filter. Control experiments established that photolysis rate is maximized when irradiation wavelength is < 300 nm. Typical irradiation times ranged from 15-60 min at a distance of about 15 cm. The photolyzed samples were then transferred to the ESR cavity of a Bruker ESP-300 ESR spectrometer (X-band, 9.608 GHz) for examination -- no loss of signal intensity was observed at 77 K for any of the cases studied.

RESULTS: Figure 1 shows example ESR spectra obtained upon photolysis of compounds 1-3, as well as diphenyl carbonate 4. Dominant features in these spectra are the monoradical spectra centered at 3425 G ($g \sim 2.0$). We observe similar monoradical spectrum peak shapes upon photolysis of the BAO's in poly(methyl-methacrylate) (PPMA) matrix. In addition to the monoradical peaks in each case are additional peaks exhibiting splitting about the $g \sim 2.0$ position that is far too large to be reasonably attributable to hyperfine interaction. These additional peaks appear to be unique to the neat solid powder or crystal samples, although the breadth of glassy matrix ESR spectra may mask radical pair triplet spectral features from irradiation of BAO's in PPMA. ⁴ The figure also shows the greater

Figure 1 : ESR SPECTRA OF NEAT SOLID BIS-ARYLOXALATES IRRADIATED AT 77 K.



Spectra 1-3 are of neat powder samples, spectra 4-5 are taken for crystalline samples aligned with long axes approximately parallel to the sample tube. Triplet radical pair transitions are marked with "T". Peaks marked "X" or "H" are due to impurities unrelated to the phenoxyl radicals.

strength of the broadly split lines in the crystalline samples (labelled T) relative to those in the irradiated powder samples.

DISCUSSION: We attribute the additional neat solid-state ESR peaks to triplet transitions due to spin-pairing interactions between geminate phenoxy radicals. Previous workers have attributed similar sets of peaks in γ -radiolysis of diphenyl carbonate to related geminate phenoxy-phenoxy pairs.⁵ Although these workers were not able to observe the radical pair spectra under photolytic conditions, we clearly observe the same radical pair triplet spectrum under our single-crystal photolytic conditions, as observed in the γ -radiolysis. It seems likely that the earlier work simply did not detect the triplet ESR spectra with the powder-sample photolytic conditions they employed, since we noted that powder samples gave only very weak triplet spectra on the outlying portions of the central radical spectra. Far more clearly we observe strong triplet peaks in our single-crystal samples of diphenyl carbonate, and in addition are able to observe some hyperfine splitting in one of the triplet transitions (see Figure 1). The hyperfine interaction in the triplet spectrum of diphenyl carbonate, as well as the solid state spectrum anisotropy as a function of crystal orientation relative to the magnetic field, are under further investigation at present by ourselves in collaboration with Dr. M. Dale Pace of the Naval Research Laboratory, and will be reported upon in future work.

Given the clear precedent of the diphenyl carbonate work, we feel quite confident of our corresponding assignment of the similar bands in BAO photolysis to triplet spin-coupled phenoxy-phenoxy pairs. It is notable that fairly broad triplet spectral extents are obtained in the oxalate photolyses, despite the fact that photolysis in the solid state might be expected to lead to the interposition of two carbon monoxide molecules between the geminate phenoxy radicals. The comparable breadth of the spectra for diphenyl carbonate and the oxalates implies a similar interaction strength between the radicals. Using a charge-dipole approximation⁶ of

$$\text{Spectral Width (Gauss)} = (1.39 \times 10^4 \text{ G-A}^3) \cdot g / r^3$$

($g = 2.002319$ for the free electron, $r =$ the average distance between electrons in the charge-dipole approximation) and estimating D -values of 40-60 Gauss for spectral widths of 80-120 G in the triplet radical-pair spectra generated from compound 2, we find the radical centers to be about 6.1-7.0 Å apart. Some orientation effects may alter this number, and we are at present attempting to obtain X-ray crystallographic analyses of the crystalline BAO samples to better define the geometry that a geminate radical pair might be expected to adopt in these molecules. For the diphenyl carbonate

photolyzed sample, a spectral width of 145 G was found, implying $r = 5.8 \text{ \AA}$.⁵ Overall, it seems clear that -- in these samples studied, at least -- there is little difference in the degree of ferromagnetic coupling that may be achieved in geminate pairs generated from a diphenyl oxalate vs. a diphenyl carbonate. In addition, we see similar sets of weak triplet radical pair peaks in all neat BAO solid state photolyses, with similar lineshapes and spectral widths regardless of the substituent patterns of BAO's studied to date.

The stability of the signals in samples without 2,6-di-*tert*-butyl stabilization is limited. The radical and triplet ESR spectra in photolyzed diphenyl carbonate crystals disappear irreversibly upon warming to room temperature, in agreement with the observations in the earlier, radiolysis work.⁵ However, over the temperature range from 12 K to room temperature, the triplet signals from **2** are persistent and change only slightly with warming and recooling to 77K.⁷ After some days under vacuum at room temperature, signals attributable to 2,4,6-tri-*tert*-butyl phenoxy triplet radical pairs are still clearly observable!! This is remarkable, since it shows that intermolecular ferromagnetic coupling between sterically stabilized phenoxy radicals is possible in the solid state, when the radicals are *generated* in the solid state, rather than generated in solution and frozen or precipitated into the solid state.

CONCLUSIONS: Although complete analysis of the ESR characteristics of phenoxy-phenoxy triplet radical pairs in BAO's is not yet complete, it is clear that this photochemical method of solid-state radical generation has promise for production of reasonably high radical concentrations, which may undergo intermolecular interaction when forced into appropriate orientation under particular solid-state conditions. Given the ease and synthetic adaptability of this method, and the reproducibility of the ESR results obtained, we consider the BAO's to be highly promising model systems as part of our search for materials with potential use for organic information storage capability.

[This work has not yet been submitted for publication, pending completion of further ESR analysis in the solid state, and of Curie Law analysis of the triplet pair spectra to estimate a lower bound on the triplet-singlet energy gap of the intermolecular spin-coupling.]

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