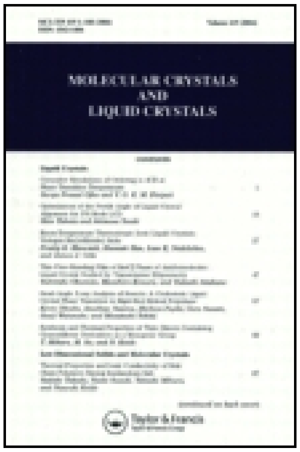

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Electron Spin Resonance of the Triplet State of a Photochemical Oxidation Product of Crystalline Durene

Mark Sharnoff [a]

[a] Department of Physics, University of Delaware, Newark, Delaware, 19711

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Electron Spin Resonance of the Triplet State of a Photochemical Oxidation Product of Crystalline Durene

MARK SHARNOFF

Department of Physics
University of Delaware
Newark, Delaware 19711

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Abstract—An optical method of detection of electron spin resonance of metastable states has permitted the investigation of the triplet entity responsible for the blue component in the phosphorescence of purified crystalline durene. This entity has fine structure parameters

$$D/hc = \pm(0.335 \pm 0.003)\ \mathrm{cm}^{-1}$$

and

$$E/hc = \mp(0.043 \pm 0.002)\ \mathrm{cm}^{-1}$$

The principal axes of the fine structure tensor and the magnitudes of its principal values are consistent with Sponer and Kanda's attribution of this phosphorescence to an aldehydic photo-oxidation product of the durene molecule.

Introduction

Monocrystalline durene has been widely used as a matrix in which aromatic solute molecules could be studied spectroscopically in the "oriented gas" phase. McClure inaugurated the use of durene for this purpose with his optical investigations of naphthalene in durene,[3,4] and Hutchison subsequently used durene as a matrix for his pioneering ESR study of the triplet state of naphthalene.[1,2] While some optical work with durene matrices continues,[5,6] the principal application of the durene crystal in recent years has been in the domain of magnetic resonance. Quinoxalene,[7] quinoline,[8] isoquinoline,[8] cinnoline[8] and tetramethylpyrazine[9] have proved amenable to the durene host and their triplet state ESR signals have, with the exception of tetramethylpyrazine, exhibited nicely resolved hyperfine structure.

These molecules practically exhaust the list of species which are small enough to enter durene readily and yet whose triplet states are sufficiently long lived (*ca.* 0.1 sec) in that lattice to be observable by the conventional methods of electron spin resonance. However, recent application to metastable triplet states[10,11,12] of optical methods of detection[13,14] of ESR have made the magnetic resonance of short-lived triplet species accessible to study,[15] and it may be anticipated that durene may once again become popular as a host matrix for studies of the paramagnetism of triplet species. With this application in view, we have carried out an ESR investigation of monocrystalline durene in order to characterize whatever background magnetic resonance there might be which could be mistaken for the triplet state ESR of a solute species intentionally introduced into the crystal.

Experimental

Purified crystalline durene emits a weak phosphorescence which cannot be attributed to the perfect crystal[16] and which thus betokens the presence of a triplet impurity. We have used intense ultraviolet irradiation to induce this impurity phosphorescence in our own crystals, where it has a lifetime of 33 ± 5 milliseconds, and have utilized it in detecting optically the ESR of the triplet species which emits it. Our apparatus was a K-band modification of a system described elsewhere.[10,15] The samples were immersed in boiling helium and irradiated continuously with filtered light from an OSRAM HBO 200 W/2 mercury lamp and with pulsed microwaves at a carrier frequency of 26.4 GHz. The repetition rate of the microwave pulses was 20 Hz. The 4141 Å or 4326 Å bands of the phosphorescence were monitored during the pulsed microwave excitation, saturation of the $\Delta m = \pm 1$ and $\Delta m = \pm 2$ ESR transitions becoming evident, at resonance, by the corresponding modulation which they produced in the phosphoresence bands. There were two complete sets of ESR transitions, indicating that there were but two magnetically distinct sites of emission of the blue phosphoresence. That the sites were substitutional may be inferred from the variations in the transition fields as the external magnetic field was rotated in the *ab*-plane of the durene host; extrema in the field strengths occurred when the field made angles of 47° or 43° with the durene *b*-axis, which correspond closely with the angles of 49° and 41° which the durene *z*- and *x*-axes make with the *b*-axis.[3]

From the angular variation patterns produced by rotation of the external magnetic field in this and in other planes, the triplet nature of the paramagnetic state could be confirmed. If the results are fitted to a spin-Hamiltonian of the usual form,[3] the values of D/hc and E/hc are $\pm(0.335 \pm 0.003)\ \mathrm{cm}^{-1}$ and $\mp(0.043 \pm 0.0020)\ \mathrm{cm}^{-1}$, respectively. The *z*-axis of the fine structure tensor lies within a few degrees of the durene *y*-axis,[3] while the *x*- and *y*-axes of the tensor correspond closely in direction to the *x*- and *z*-axes[3] of the durene, respectively. The uncertainties listed for D and E arise primarily from unreliability in the orientation of our crystals, our mounting techniques permitting at present an uncertainty of no less than 4° in the alignment of a given lattice vector with the normal to the plane in which the external magnetic field is rotated. Additional uncertainties are occasioned by the large linewidths of the signals, which ranged from 45 gauss to 85 gauss full width at half maximum intensity, depending upon the orientation of the magnetic field.

We observed no resolved hyperfine splitting of the ESR transitions, although the pervasive symmetry (Fig. 1) of the signals suggests that the major source of linewidth[17] is the hyperfine interaction. (Had the linebreadths arisen mainly from inhomogeneity of the crystalline field, with concomitant variations of the fine structure tensor from site to site, the signals would have been noticeably asymmetric, particularly at orientations at which extrema in the fine structure patterns occurred.) We estimate that a steady state population of about 10^{10} triplets was achieved in these experiments.

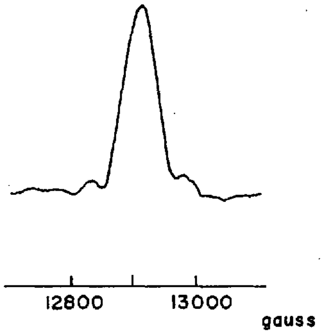

Figure 1. Optically detected ESR absorption signal, obtained with magnetic field approximately parallel to the z-axis of the paramagnetic species. Microwave frequency, 26.31 GHz. Temperature, 1.8°K.

Discussion

From the presence of a distinct 1700 cm^{-1} vibrational mode in the impurity phosphorescence of crystalline durene (and in crystals of other methylated benzenes), Sponer and Kanda have argued[16] that this emission originates from an aldehyde, presumably a benzaldehyde derivative formed photochemically from oxygen occluded in the crystalline lattice. Our experience with crystalline durene substantiates this point of view in several respects. Firstly, we found that crystals freshly grown in vacuum from a melt of degassed and extensively zone-refined starting material did not exhibit the impurity luminescence reported by Sponer and Kanda, but rather, after extensive UV irradiation, a finely structured and short-lived (less than 1 millisecond) green luminescence whose origin lay at 20 410 cm^{-1}. Similar crystals which had been exposed to air for several weeks behaved like the solution-grown crystals of Sponer and Kanda, however, the blue luminescence being emitted fairly uniformly throughout the crystal. Secondly, the fine structure parameters D and E of the species responsible for the blue phosphorescence are much larger than expected for aromatic π–π^* triplets[18,19,20] and are of about the magnitude which one might expect for an n–π^* triplet which is conjugated, such as might occur for a carbonyl group in benzaldehyde. Thirdly, the contribution of only two magnetically distinct sites to our ESR signals shows that the impurity and the processes by which it is produced involve the regularity of structure of both the durene molecule and of the durene crystal.

A heuristic analysis, based upon Van Vleck's observation[17,21,22] that the secular terms in the magnetic dipolar interaction of two electrons both have a $(3 \cos^2 \delta - 1)$ variation with the angle δ, between the magnetic field and the interelectron radius vector, and upon the qualitative form of the wavefunction of an n–π^* triplet whose unpaired electrons occupy, respectively, a C–O π-antibonding orbital and in-plane primarily O non-bonding π orbital, suggests that the fine-structure splitting of a conjugated n–π^* carbonyl triplet would be maximized when the external magnetic field is parallel to the carbonyl bond, minimized when it is perpendicular to the carbonyl bond but parallel to the plane of the CHO group, and at an intermediate value when it is perpendicular to the plane of the CHO group. The data given above thus suggest that the carbonyl bond of our hypothetical aldehyde triplet is approximately parallel to the durene y-axis, the plane of the CHO group being parallel to the plane of the durene ring. This is, however, just the situation which would obtain if any of the methyl groups of the durene were replaced by a CHO group whose orientation (Fig. 2) were " natural " in view of conjugative, steric, and hydrogen-bonding effects. Such a configuration implies only two orientations of the aldehyde.

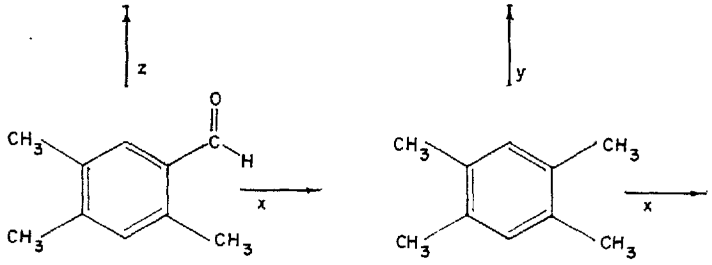

Figure 2. Proposed structure and orientation, relative to a durene molecule, of the molecule responsible for the blue luminescence of crystalline durene.

We believe that this is the first reported observation of the ESR of a carbonyl triplet state.

Acknowledgment

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