Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Paramagnetic Species in Gamma-irradiated Durene Crystals at Room Temperature

J. L. Monge [a] & M. Schott [a]
[a] Groupe de Physique des Solides de l'Ecole Normale Supérieure Tour, 23 9 quai St-Bernard, Paris, 5e

Version of record first published: 28 Mar 2007.

To cite this article: J. L. Monge & M. Schott (1970): Paramagnetic Species in Gamma-irradiated Durene Crystals at Room Temperature, Molecular Crystals and Liquid Crystals, 10:4, 389-397

To link to this article: http://dx.doi.org/10.1080/15421407008083500

Molecular Crystals and Liquid Crystals. 1970. Vol. 10, pp. 389–397

Paramagnetic Species in Gamma-irradiated Durene Crystals at Room Temperature

J. L. MONGE and M. SCHOTT

Groupe de Physique des Solides de l'Ecole Normale Supérieure†
Tour 23
9 quai St-Bernard
Paris 5e

Received February 9, 1970; *in revised form April* 27, 1970

Abstract—The study of the EPR spectrum of γ-irradiated Durene single crystals shows the presence of at least four radicals, three of which are tentatively assigned to tetramethylcyclopentadienyl, tetramethylcyclohexadienyl, and 2-4-5 trimethylbenzyl.

It has been known for a long time that a green luminescence is obtained in Durene, either crystalline or dispersed in a rigid matrix, upon irradiation with UV light, or X- or γ-rays.(1) All the known properties of this luminescence are in agreement with the assignment of this emission to the radical 2-4-5 trimethylbenzyl.(2) An EPR absorption should therefore be seen in irradiated Durene, and was indeed found by Martin-Bouyer.(3) We have studied the EPR spectrum of pure Durene crystals irradiated with γ-rays (^{60}Co) and UV light at room temperature. An EPR absorption spectrum is very easily obtained, but it is actually composite and many radicals contribute, as shown by its progressive change of shape upon annealing, or with increased microwave powers. We discuss below possible identifications of three radicals, present just after irradiation.

Radical I

During the first three days after irradiation, at room temperature, the most prominent features are 12 equidistant lines, each about 2 Gauss wide, spaced by 6.4 ± 0.2 Gauss (depending on orientation),

---

† Laboratoire associé au C.N.R.S.

superimposed on a broad structureless absorption only clear at very low microwave powers (see below, radical III). This seems to be the already published spectrum,⁽⁴⁾ although the spacing quoted there is 6.72 G. In addition, two very weak lines are present, one on each side of the spectrum, about 6.4 Gauss from lines 1 and 12; their intensity is about $\frac{1}{10}$th of that of lines 1 and 12, and they behave exactly as the 12 main lines as regards microwave power. They can be observed after radical II has been bleached by light (this process will be discussed elsewhere) (Fig. 1). The relative heights of the lines are not known precisely due to the presence of other radicals, which is difficult to correct for, but they seem to follow a binomial law for 13 equivalent protons only approximately. The spectrum is slightly anisotropic, the spacing of the lines varies slightly with orientation. This is in disagreement with statement of complete isotropy,⁽⁵⁾ but this was not studied in details. It is also slightly unsymmetric around its center.

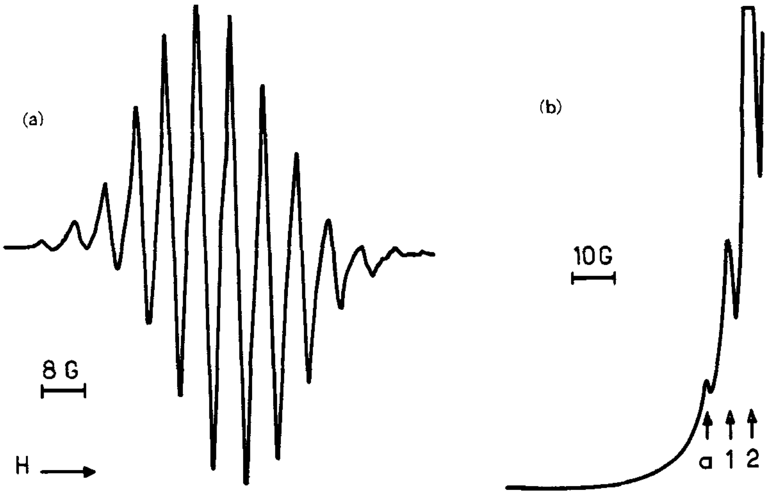

Figure 1. X-band EPR spectrum of a γ-irradiated Durene crystal, after bleaching of radical II. Approximate dose 2.10^{20} eV/cm^3. (a) Twelve main lines; (b) the low-field side of the same spectrum showing the small line *a*.

This points towards a radical with 13 equivalent protons. The 2-4-5 trimethylbenzyl indeed contains 13 protons. Although not explicitely stated, this assignment seemed favored by others,⁽⁴,⁵⁾ who compared the present spectrum with a 12-lines spectrum attributed to the Durene cation radical,(6) and suggested that the missing hydrogen might well be one of a methyl group. In our opinion, this is not possible. The 13 protons of 2-4-5 trimethylbenzyl cannot be all equivalent—or almost—for all directions of the applied field in the Durene single crystal where the radicals are at most very slightly displaced from one of the two non-equivalent positions of a Durene molecule in the crystal (monoclinic). Moreover, this signal does not change with time like the green fluorescence of the radical excited in its own doublet-doublet first absorption band at 4800 Å. This, however, is not clear cut, as quantitative measurements on the green fluorescence are made difficult by reabsorption in the most heavily irradiated samples, and by variation of the radical lifetime from place to place in the crystal, may be due to oxygen diffusion. For instance radical I, when generated by UV light, near the surface, decays more rapidly than when generated by γ-rays, in the bulk.

Another possible assignment is to tetramethylcyclopentadienyl, with perhaps some admixture of the trimethyl analog, which would account for the disagreement with the binomial law. Ring contraction of a benzene derivative to a cyclopentadienyl is a known photochemical process(7) in the vapor phase. Electron or UV irradiation of cyclopentadiene(8,9) or benzene(10) at 77 °K generates a radical having a well-resolved sextet spectrum which is assigned to C_5H_5. Its splitting is 5.6 G,(8) 6.2 G(9) or 5.9 ± 0.3 G,(10), to be compared to our value of 6.4 ± 0.2 G.

The radicals, being slightly smaller than the Durene molecule, could undergo a reorientation in their planes, of which there are two unequivalent in the crystal. Molecular reorientations are already known in the crystals of some Durene derivatives.(11) However, the five ring carbons should in addition have equal spin densities, and this is far from evident in substituted cyclopentadienyls, where methyl substitution destroys the ground state degeneracy. Calculations still in progress fail up to now to give equal spin densities, and our assignment is therefore only tentative.

Radical II

Another spectrum is visible in the wings of radical I. It is more easily saturated (Fig. 2) and much more anisotropic than spectrum I. It is formed of a large number of lines, each about 1.5 G wide. In certain directions these lines are distinct and spaced by about 2.5 to 3 G. In others, they collapse in four groups, spaced by about 10 G, whose relative intensities are approximately 1, 1, 0.6 and 0.2. This structure is clearer in K_a band (Fig. 3). The sensitivity in X band is too low, so the field modulation amplitude which must be used is too large, and only four wide lines appear, with sometimes an unresolved structure (Fig. 2). The distance between the centers of the pairs of equal lines on both sides of spectrum I, is about 96 ± 4 G.

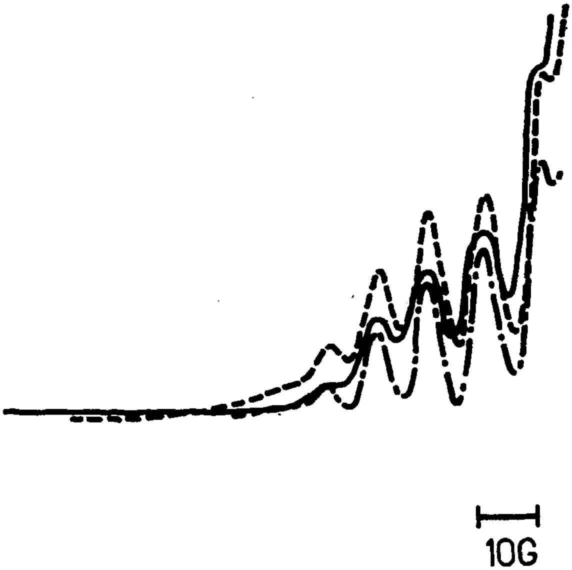

Figure 2. Saturation behaviour of radical II. X-band spectrum on Varian V 4502, depending on attenuation: —— 10 db; — — 15 db; — · — 20 db. The line at extreme right is line 1 of radical I, line *a* being invisible here.

This suggests a radical containing either one proton at 96 G or two protons at 48 G, plus seven protons at 10 G (assuming the presence of a weak undetected fifth line) and in addition other equivalent protons with a much smaller coupling constant of about 2.5 G to 3 G, which could be the tetramethylcyclohexadienyl radical (Fig. 4).

The published values of the protons coupling constants in cyclo-

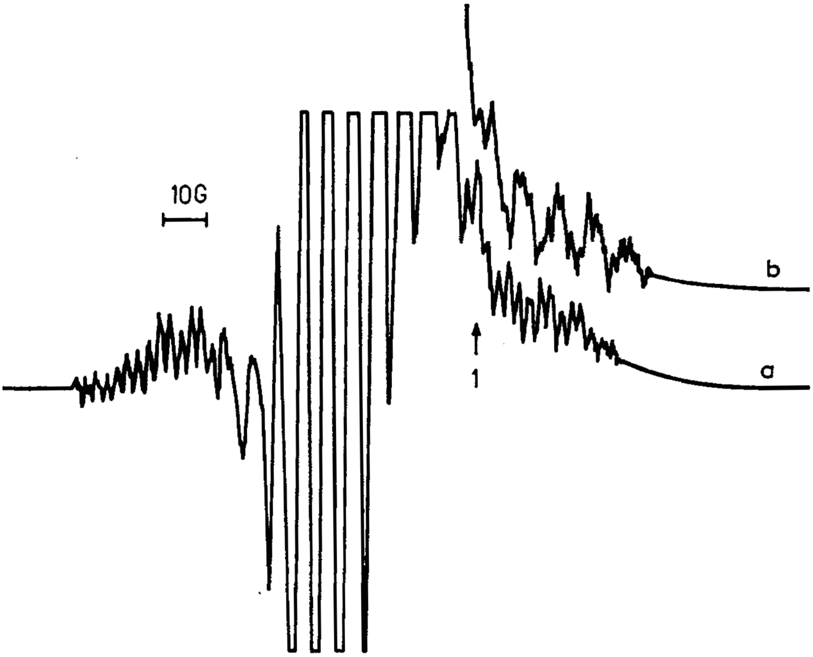

Figure 3. K_a-band spectrum showing a more detailed structure in radical II and the influence of the direction (unknown) of static magnetic field vs crystal axes. a–b: different crystal directions. 1: line 1 of spectrum I.

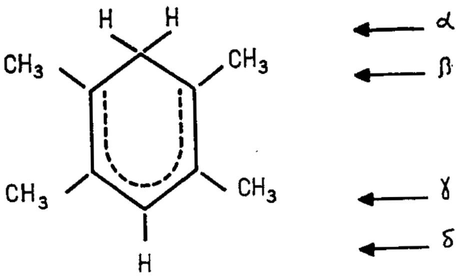

Figure 4. Tetramethylcyclohexadienyl radical.

hexadienyl radical vary somewhat: 47.5 Gauss in $\alpha^{(12,13)}$; $9^{(13)}$ or $10.4^{(12)}$ in β; about 2.5 Gauss in $\gamma^{(12,13)}$; $10.4^{(12)}$ or $13^{(13)}$ in δ. The methyl substitution will increase the coupling constants of the methyl protons over those of the unsubstituted protons. The ratio of the McConnell constants is about 1.25, so there will be little difference between the methyl protons in β position and the proton in δ. A more detailed comparison with experiment is not possible, as only a small part of this spectrum is accessible, and the anistropy could not be investigated further.

The formation of a cyclohexadienyl by attachment of a H atom to the cycle of a methylated benzene is known in methanol at 77 °K for instance,(14) and at room temperature in γ irradiation of other solid substituted benzenes and of biphenyl.(15)

The most natural assignment of spectrum II is to the above radical, formed by addition of a H atom, abstracted from a neighboring Durene molecule, a process likely to occur in the solid. As this assignment is based on the knowledge of part of the spectrum only, and as this substituted cyclohexadienyl has not been studied otherwise, it must be considered only tentative.

Radical III

None of the previous spectra can be associated with 2-4-5 trimethylbenzyl (radical III), although a large quantity of it is certainly present initially, as shown by the intensity of the green fluorescence. We already noted the presence of a broad structureless absorption at low microwave powers. Studying the dispersion, we found a signal, larger than any of the other signals in absorption. It is a structureless spectrum of width about 90 G.

This is what is expected for radical III: from the known benzyl coupling constants, one expects six different kinds of protons; even the ortho and para positions will have different coupling constants, as in benzyl, or in substituted phenoxy radicals.(16) This leads to 768 lines in 90 G: hence no observable structure.

The dispersion signal decays with time after irradiation as does the green fluorescence when excited in the first absorption band of radical III. This broad structureless spectrum is therefore likely due to the 2-4-5 trimethylbenzyl radical.

Initially, the signal is so intense, that it is not necessary to stabilize the Klystron frequency through an auxiliary cavity. Although the noise level is then very high, a dispersion signal is immediately obtained.

Other Species

These are not the only radicals present in the Durene matrix at some stage of its evolution after irradiation. For instance, yet another radical is present, may be already just after irradiation. It is most easily observed after two hours annealing at 330 °K, its lifetime being much longer than those of the radicals discussed above. Its spectrum is made of 8 lines with approximate intensities 1-4-6-5-5-6-4-1 and might correspond to one proton at 19.5 ± 1 G and four protons at 6.3 ± 0.3 Gauss. Consequently, this radical perturbs spectrum I, whose observation is made difficult at long times, and on the other hand, its study just after irradiation is difficult, due to the presence

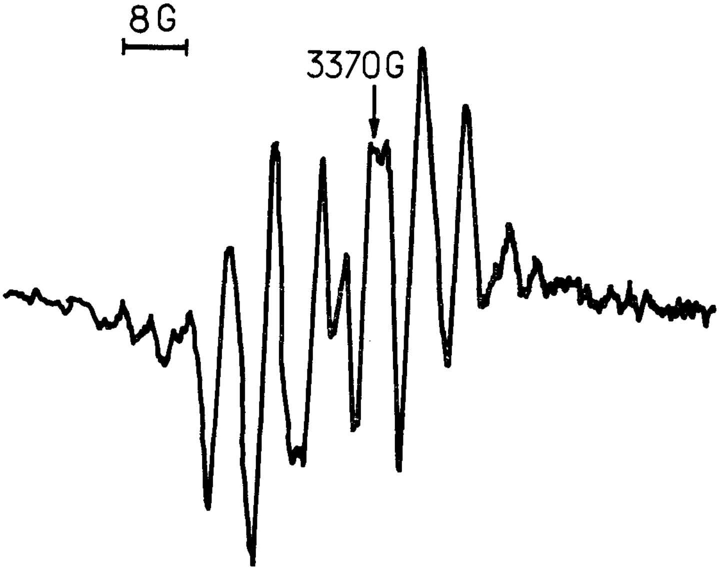

Figure 5. X-band spectrum of a γ-irradiated Durene crystal, after 16 hours annealing at 60 °C (melting temperature 80 °C). Approximate dose 6.10^{20} eV/cm^3.

of a prominent spectrum I. It is not clear whether this 8-lines spectrum is due to a radical present from the beginning, or the product of the evolution of some other (*s*) species. (Fig. 5).

We shall not discuss here the further chemical changes which take place in a Durene crystal after the end of the irradiation and whose kinetics appears to be quite complicated. New transient radicals appear, as well as stable species which appear for instance as luminescence centers. Impurities, especially oxygen, play a role in these last steps. For instance, one stable product has been identified as a methylated benzaldehyde, through its phosphorescence spectrum at low temperature.(17) The processes leading to radicals I, II and III might be on the contrary primary processes, which take place in the Durene molecule at the time of irradiation. These radicals are protected in the crystalline matrix, which slows down considerably the chemical processes. In a crystal which has been kept at room temperature, an EPR absorption is still detectable more than a month after the end of the irradiation, it is then dominated by the last spectrum described (a doublet of quintuplets).

Acknowledgement

This work was supported in part by the D.G.R.S.T. under contract 66.00.299.01.

REFERENCES

1. Goldstein, E., *Verh. Deutsch. Phys. Ges.* **13**, 378 (1911); and a number of recent publications, cited in Ref. (2).
2. Leach, S. and Migyrdician, E., *Chem. Phys. Letters* **1**, 21 (1967), and *Comptes rendus* **264**, 156 (1967); Johnson, P. M. and Albrecht, A. C., *J. Chem. Phys.* **48**, 851 (1968).
3. Martin-Bouyer, M. and Fric, C., *J. Chim. Phys.* **64**, 1053 (1967).
4. Heurtaux, J. and Martin-Bouyer, M., *Comptes rendus B* **267**, 629 (1968).
5. Fric, C., Martin-Bouyer M. and Heurtaux, J., *Comptes rendus B* **268**, 694 (1969).
6. Hulme, R. and Symons, M. C. R., *J. Chem. Soc.* 1120 (1965).
7. Porter, G. and Ward, B., *Proc. Roy. Soc. A* **303**, 139 (1968).
8. Ohnishi, S. I. and Nitta, I., *J. Chem. Phys.* **39**, 2848 (1963).
9. Liebling, G. R. and McConnel, H. M., *J. Chem. Phys.* **42**, 3931 (1965).
10. Carter, M. K. and Wincow, G., *J. Chem. Phys.* **47**, 292 (1966).
11. Charbonneau, G. and Meinnel, J., *J. Chim. Phys.* **65**, 1590 (1968); Balcou, Y., Gregoire, P. and Meinnel, J., ibid. **62**, 536 (1965).

12. Ohnishi, S. I., Tanei, T. and Nitta, I., *J. Chem. Phys.* **37,** 2402 (1962).
13. Fessenden, R. W. and Schuler, R. H., *J. Chem. Phys.* **39,** 2147 (1963).
14. Leone, V. A. and Kiski, W. S., *J. Am. Chem. Soc.* **88,** 656 (1966).
15. Campbell, D. and Turner, D. T., *Can. J. Chem.* **45,** 881 (1967).
16. Stone, T. J. and Waters, W. A., *J. Chem. Soc.* 213 (1964).
17. Migyrdician, E., *Ber. Bunsen* **72,** 344 (1968); Bertault, M., Thesis, Alger 1969.