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AN EVIDENCE FOR SINGLET GROUND STATE OF 1,6-DI-t-BUTYL-3,4,8,9-TETRAPHENYLTRICYCLO[6.2.0.$0^{2,5}$]DECA-1,3,5,7,9-PENTAENE

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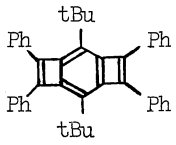
Ground state of the title compound (1) was shown to be singlet by means of its ESR spectrum and magnetic susceptibility.

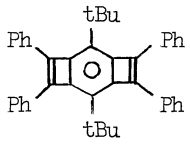
It is an interesting subject to study the ground state of the title compound (1), because it still remains undissolved that the ground state of cyclobutadiene is whether singlet or triplet.[1] Although 3,4,5,6-tetramethyl-1,2-diphenylbenzocyclobutadiene has been isolated[2] as the first example of benzocyclobutadiene, neither its ESR spectrum nor magnetic susceptibility has been reported.[3] We wish to report magnetic susceptibility and ESR spectrum of 1 which has been isolated as deep blue needles by a novel thermal cycloaddition reaction of E,E-3,4-bis(t-butylphenylethynylmethylene)-1,2-diphenylcyclobut-1-ene.

The magnetic susceptibility[4] of 1 was measured in the temperature range 55-300°K. The data thus obtained were corrected for the diamagnetic contribution of $\chi_{dia} = -0.362 \times 10^{-3}$ emu/mol calculated by the Pascal's method. The result showed that the susceptibility is temperature-independent and that the paramagnetic contribution from 1 is almost negligible. Therefore, 1 would exist in the singlet ground state (S=0) and, at least, the triplet state of 1 would not be detectably populated alongside the singlet state below 300°K.

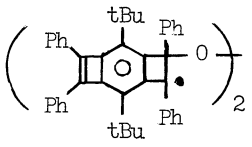
On the other hand, 1 showed an isotropic ESR signal[4] in crystalline state at room temperature. G-value and line width were 2.0032 and 5.44 gauss, respectively. This g-value is very similar to



(1)



(2)



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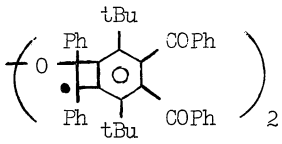

(4)

those of usual organic free radicals. The blue color of 1 changed gradually to yellow color at room temperature in the air. As the color change proceeds, the intensity of the isotropic ESR signal increased. However, 1 which was freshly prepared in a degassed sealed glass tube showed very weak ESR signal. Therefore, the ESR signal is not attributable to the triplet state of 1, but probably due to radical intermediate including oxygen atom. Plausible radical intermediates are 3 and/or 4 which was produced by the reaction of 1 and oxygen, because 1 was easily oxydized in the air to afford 1,2,4,5-tetrabenzoyl-3,6-di-t-butylbenzene as yellow prisms.[3] However, ESR hyperfine splitting could not be observed, because of very low solubility of 1 in usual organic solvents.

Finally, the deep blue color of 1 which shows the visible absorption bands in $CHCl_3$ at 394 and 643 nm, is not attributable to its radical structure, but probably to an electronic excitation from its singlet ground state. Because it has been reported[6] that the resonance stabilization of benzocyclobutadiene can not be expected, the most important canonical structure of 1 is to be 2. Therefore, the ground state of 1 would be well presented by the structure 2.

References

1) See, e.g., G. Maier, Angew. Chem. Intern. Ed., 13, 425 (1974).

2) H. Straub, ibid., 13, 405 (1974).

3) F. Toda and M. Ohi, Chem. Commun., in press.

4) Magnetic susceptibility measurements were carried out with a Shimazu ME-2 type magnetic torsion balance, equipped with a low temperature crystat. All the ESR measurements were carried out using a JES-ME-3X spectrometer equipped with Takeda-Riken microwave frequency counter. ESR line width and g-value were measured relative to those of $(KSO_3)_2NO$ ($a^N = 13.05 \pm 0.03$ gauss; $g = 2.0054$[5]).

5) J. J. Windle and A. K. Wiersma, J. Chem. Phys., 39, 1139 (1963).

6) A. Y. Meyers, Tetrahedron, 26, 6215 (1968), and references cited therein.

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