Electrical Conductivity of α, α′-Diphenyl-β-picrylhydrazyl under High Pressure

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Recently, several examinations of the effect of pressure on such molecular crystals as polycyclic aromatic compounds, have been reported.[1,2,3] As a function of the intermolecular distance, in this article we will present the effect of pressure on the electrical conductivity of the organic free radical, α, α'-diphenyl-β-picrylhydrazyl (DPPH), and also on that of some polycyclic aromatic compounds.

The electrical resistance cell employed consisted of a cylinder and two opposed pistons of Carboloy, with truncated cone ends and press-fitted in hard-steel outer jackets. The specimen (1.2 mm. in diameter and 0.08 mm. thick), encased in a pellet of pyrophyllite, was compressed between the flat centre sections of the pistons.[4] The piston was electrically insulated from the press with mica. Because of the fairly low insulation of the high pressure cell itself, $10^7\ \Omega$, it was not possible to measure the resistivity of the specimen above $10^7\ \Omega$cm. An appropriate apparatus for the measurement of a high resistance, up to $10^{11}\sim10^{12}\ \Omega$, with a boron nitride pellet is now being prepared.

The abrupt change in the electrical resistance of bismuth or lead at a phase-transition point was used to calibrate the pressure applied to the cell. The transition of bismuth occurs at 2.5×10^4 kg./cm^2 and 8.8×10^4 kg./cm^2, and that of lead, at 1.61×10^5 kg./cm^2.

1) H. Inokuchi, This Bulletin, **28**, 570 (1955).
2) R. S. Bradley, J. D. Grace and D. C. Munro, *Trans. Faraday Soc.*, **58**, 776 (1962).
3) G. A. Samara and H. G. Drickamer, *J. Chem. Phy.*, **37**, 474 (1962).
4) A. S. Balchan and H. G. Drickamer, *Rev. Sci. Inst.*, **32**, 308 (1961).

A sharp drop in the electrical resistance of the purified free radical[5] was found at a lower pressure range, 10^4 kg./cm^2, as is illustrated in Fig. 1. The atmospheric resistivity of DPPH was found to be 10^{13} Ω cm. at room temperature.[5]

The behaviour was reproducible, and no chemical change could be found under high compressiron. Under the high pressure, the molecules are brought closer together, and this leads to a larger molecular orbital overlap between neighbouring molecules. A quantitative treatment with a band theory for this increments of the overlapping of molecular orbitals will be reported elsewhere.[6]

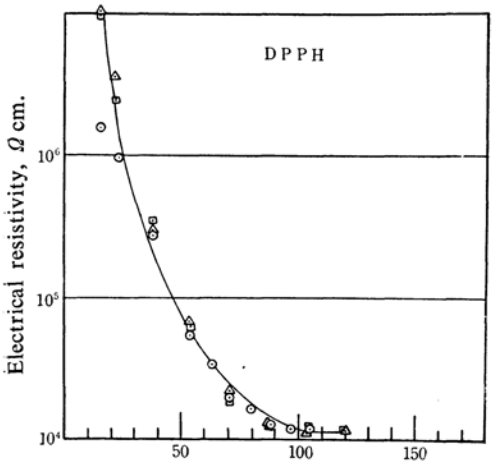

Fig. 1. The resistivity change of DPPH under high pressure.
Different marks, △ ⊡ ⊙, are shown different specimens of the free radical.

5) H. Inokuchi, Y. Harada and Y. Maruyama, This Bulletin, 35, 1559 (1962).

No chemical reactions among the free radical molecules were found under the compression of 10^5 kg./cm^2. A further compression, however, may induce a solid phase reaction in the D. P. P. H. crystal. A similar result for several organic semiconductors, violanthrone, pentacene and quaterrylene, was obtained as illustrated in Table I.

TABLE I. THE SEMICONDUCTIVITY ($\rho=\rho_0\cdot\exp(\Delta\varepsilon/2kT)$) OF POLYCYCLIC AROMATIC COMPOUNDS UNDER A HIGH PRESSURE

Compound	At atmospheric pressure		at 1.6×10^5 kg./cm^2	
	$\rho_{15°C}$**	$\Delta\varepsilon$**	$\rho_{15°C}$**	$\Delta\varepsilon$**
Quaterrylene	1.2×10^8	0.60	6×10^3	0.16
Violanthrone	2.3×10^{10}	0.78	7×10^2	0.18
Pentacene*	10^{14}	1.5	6×10^3	0.14

* A decomposition of the compound under a high pressure may occur.
** $\rho=\Omega$ cm. and $\Delta\varepsilon$=eV.

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6) Y. Harada, Y. Maruyama, I. Shirotani and H. Inokuchi, This Bulletin, in press