CHEMISTRY LETTERS, pp. 733-735, 1972. Published by the Chemical Society of Japan

HEAT CAPACITY ANOMALY IN THE CRYSTALLINE ORGANIC FREE RADICAL, p-Cl-BDPA

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The heat capacity has been measured on polycrystalline sample of 1,3-bisdiphenylene-2-p-chlorophenyl-allyl (abbreviated as p-Cl-BDPA). The sharp heat capacity anomaly was observed at 3.25 K, which may imply a paramagnetic-antiferromagnetic phase transition. This phenomenon accords well with the other results obtained from the susceptibility, ESR, and NMR measurements.

The magnetism of organic free radicals is being watched with keen interest. The aromatic free radical, 1,3-bisdiphenylene-2-phenyl-allyl (BDPA), is one of the subjects of extensive study. BDPA may be the only known example of an organic crystal which undergoes a magnetic phase transition from a paramagnetic to an antiferromagnetic state, as has been pointed out by Hamilton and Pake.[1] Recently, Duffy et al. have strongly supported the aforementioned fact by the susceptibility and heat capacity measurements.[2] While, previous to their work, one of the present authors has discussed in detail on the magnetic properties of organic free radicals and concluded that the neutral organic free radicals with one unpaired electron in a molecule have a one-dimensional antiferromagnetic spin array with a Heisenberg type isotropic exchange interaction, the data on two organic free radicals, BDPA-Bz and p-Cl-BDPA, are considered to imply a long-range ordering of electron spins at the Néel temperature of 1.78 K and 2.8 K respectively.[3]

In this communication, we would like to report on a result of a heat capacity measurement of p-Cl-BDPA in the temperature range from 1.5 K to 30 K.

The sample of p-Cl-BDPA reported here is a chloro-derivative of BDPA and has a molecular structure as follows,

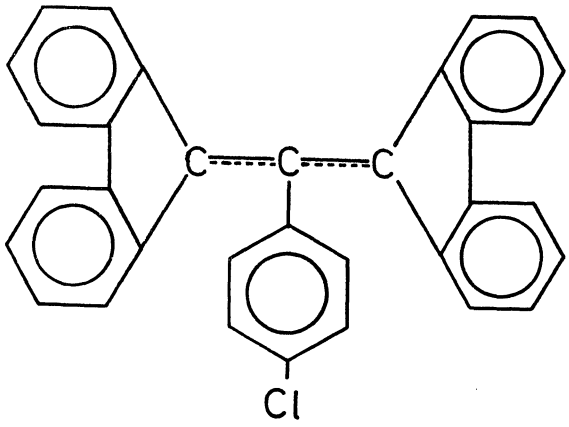

Fig. 1 1,3-bisdiphenylene-2-p-chlorophenyl-allyl

The radical was prepared according to a procedure of Kuhn and Neugebauer[4] and recrystallized from a benzene-benzine mixed solution. The precise description of the heat capacity measurement will be published succeedingly.

The heat capacity data on p-Cl-BDPA were corrected by the can heat capacity and are shown in Fig. 2.

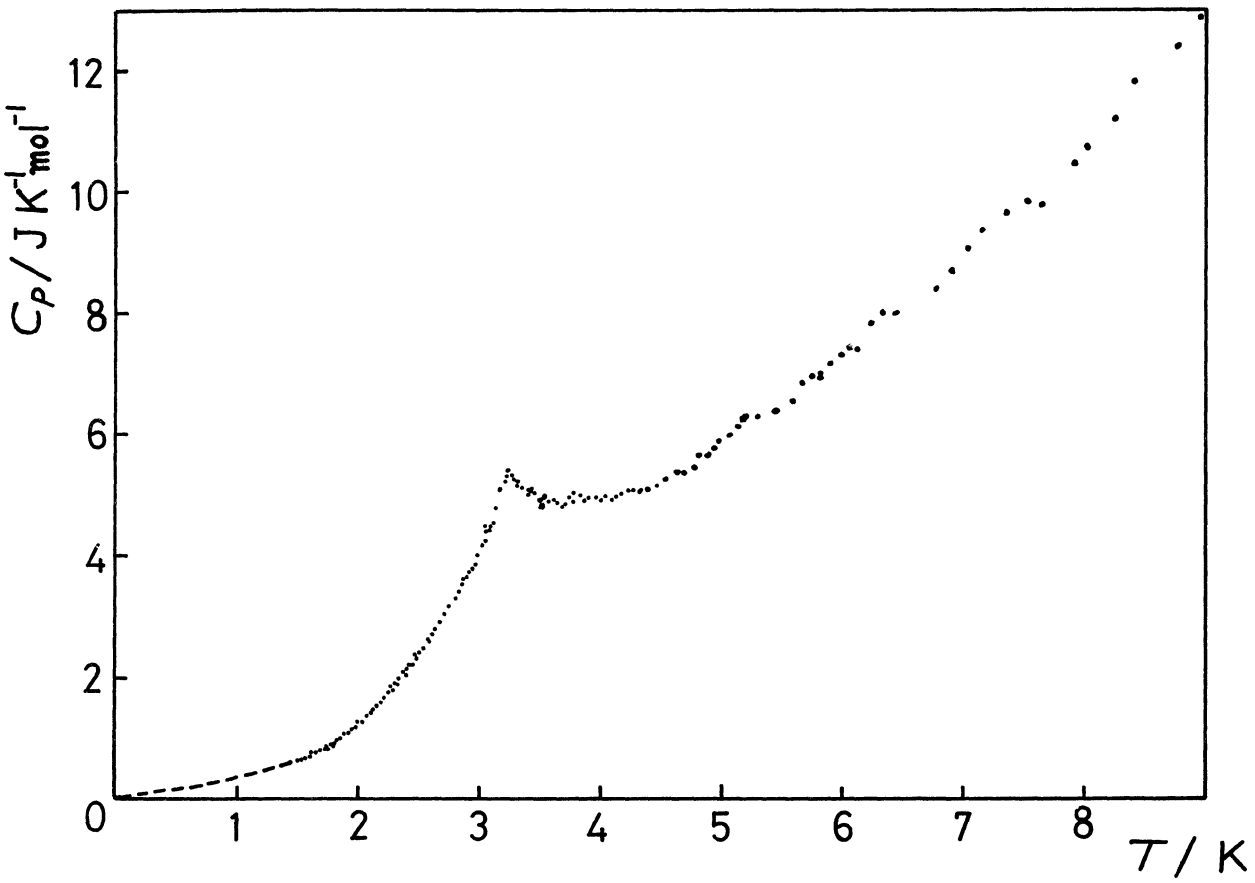

Fig. 2 Heat capacity of p-Cl-BDPA

The sample displayed a sharp peak in the vicinity of 3.25 K. This anomaly may be interpreted as caused by an onset of a long range ordering of unpaired electrons in molecules. According to the susceptibility measurement,[3] p-Cl-BDPA exhibits a broad maximum at T_m = 5.6 K owing to a short range magnetic ordering of unpaired electrons. When the temperature is decreased further, the susceptibility decreases comparatively slowly towards a finite susceptibility at T = 0 K. These phenomena are well explainable on a basis of a linear Heisenberg model and shown to be consistent with a one-dimensional magnetic chain model of an isotropic exchange interaction. However, a discontinuity in the slope of susceptibility was simultaneously found in the vicinity of 2.8 K, after which the susceptibility rises again. On the other hand, the ESR absorption line of p-Cl-BDPA broadens out and disappears as the temperature approaches 2.8 K from higher temperatures,[3] and also intensities of the NMR absorption decrease rapidly around 3.2 K.[5] The present specific heat data support strongly these phenomena and the anomaly in the heat capacity may be referred to a cooperative magnetic phase transition in the organic free radical, p-Cl-BDPA. This may be induced by a presence of a small interaction between the magnetic linear chains in the radical crystal.

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(Received June 19, 1972)