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ANTIFERROMAGNETIC RESONANCE OF ORGANIC FREE RADICAL POLYCRYSTALLINE 1,3-BISDIPHENYLENE-2-(p-CHLOROPHENYL)-ALLYL

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The paramagnetic resonance of polycrystalline 1,3-bisdiphenylene-2-(p-chlorophenyl)-allyl can be observed in the temperature region above 3.25 K. Below the temperature the anomalous resonance absorptions, which may be the antiferromagnetic resonance, were observed. This may be the first experimental observation in organic free radicals.

Recently the magnetic long range ordering of unpaired electrons in organic free radicals has been convinced by several experimental methods. One of organic free radicals which exhibit such a magnetic phase transition is a free radical named 1,3-bisdiphenylene-2-(p-chlorophenyl)-allyl (abbreviated as p-Cl-BDPA), whose molecular structure is shown in Fig. 1. The magnetic susceptibility of the powdered p-Cl-BDPA1) obeys the Curie-Weiss law with a negative Weiss constant of $\Theta = -6$ K and reaches a broad maximum at the temperature 5.6 K. Then it decreases comparatively slowly as the temperature is decreased down to about 3 K. This effect can be attributed to the magnetic short range ordering of the unpaired electrons in the crystal. On the other hand, the linewidth of the paramagnetic resonance absorptions1) increases below 5.6 K, owing to the magnetic short range ordering effect and then the absorptions disappear. These phenomena indicate the possible existence of the magnetic long range ordering of the unpaired electrons.

Recently the heat capacity measurement2) was carried out on p-Cl-BDPA and an anomaly in the magnetic heat capacity was observed at 3.25 K. The magnetic heat capacity displays a sharp peak at 3.25 K and a Schottky-type broad maximum near 5 K ; the former is associated with a magnetic long range ordering and the latter with a short range ordering in the unpaired electron spins of p-Cl-BDPA. Thus it has become clear that p-Cl-BDPA undergoes a magnetic phase transition from a paramagnetic to an antiferromagnetic state at 3.25 K.

In the proton nuclear magnetic resonance (NMR)[3] an anomaly of the absorption intensity was observed in the vicinity of the magnetic phase transition temperature. However, the shifted absorption lines in the antiferromagnetic region could not be found for powder samples.

This letter reports the anomalous resonance absorptions in the antiferromagnetic region. This may be the first experimental observation of the antiferromagnetic resonance in organic free radicals.

In the paramagnetic region the spectrum shows a very sharp absorption line owing to an extreme exchange narrowing of linewidth. At room temperature the linewidth is as sharp as 600 mG. However, in the neighborhood of the transition temperature the absorption line becomes deformed asymmetrically. This may imply that p-Cl-BDPA begins to appreciate a local field caused by a magnetic long range ordering.

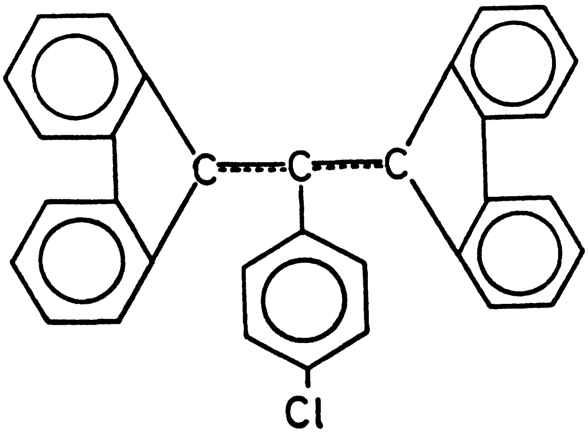

Fig. 1. Molecular structure of the radical, p-Cl-BDPA.

In the antiferromagnetic region below 3.25 K, anomalous resonance absorptions were observed. The absorptions mainly consist of three components, one in the high field side and the others in the low field side of a central paramagnetic resonance position (g=2.00, 3240 G). Figure 2 shows a spectrum obtained at the temperature 2.600 K. Very weak line can be noticed in the paramagnetic resonance position, as is indicated by an arrow. The position of this line is almost independent of temperature and coincides with the position where the paramagnetic resonance absorptions are observed above 3.25 K. Therefore, this can be attributed to a certain paramagnetic impurity in the antiferromagnetic state.

On the other hand, the other resonance absorptions are largely dependent on temperature, that is, the lower the temperature is decreased, the more the high field line shifts to a high field side and the low field lines to a low field side. The sublattice magnetization in the antiferromagnetic p-Cl-BDPA, which is obtained in a molecular field approximation by the specific heat measurement, may possibly be responsible to the large temperature dependence of the absorption spectra. Therefore,

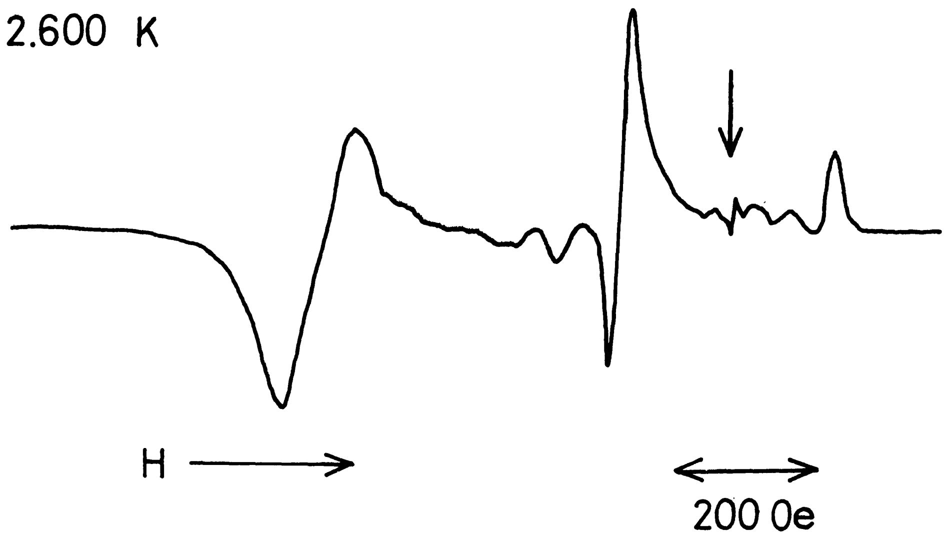

Fig. 2. Antiferromagnetic resonance absorption of powdered p-Cl-BDPA.

it may be reasonable to say that the spectra observed in the temperature range below 3.25 K are the antiferromagnetic resonance absorptions so that the resonance gives a microscopic evidence of the magnetic long range ordering of the electron spins in the organic free radical. This may be the first experimental example of the antiferromagnetic resonance in organic free radicals.

The other fine components seen in Fig. 2 may be caused by micro-crystals in a polycrystalline powdered sample. The shape of the absorptions of antiferromagnetic resonance on the present radical was dependent on a sample preparation or a sample purity. Another typical pattern is shown in Fig. 3. This spectrum contains broad absorption lines and is similar to that obtained when the anisotropy of g-values is present in the paramagnetic resonance spectra. An arrow also shows an absorption due to paramagnetic impurity. The intensity of the absorption of the impurity is larger than that in Fig. 2. The difference of the antiferromagnetic resonance absorptions in Figs. 2 and 3 is not clear at present, but it may depend on a paramagnetic impurity or a uniformity of electron spins in the antiferromagnetic state.

The temperature dependence of the shift of the resonance absorptions from a paramagnetic position gives information about a magnetic transition temperature of 3.25 K, which is in good agreement with the data of the specific heat measurement.

Three components of the absorption lines are the resonance for an external field applied along the three principal axes in the antiferromagnetic state. According to

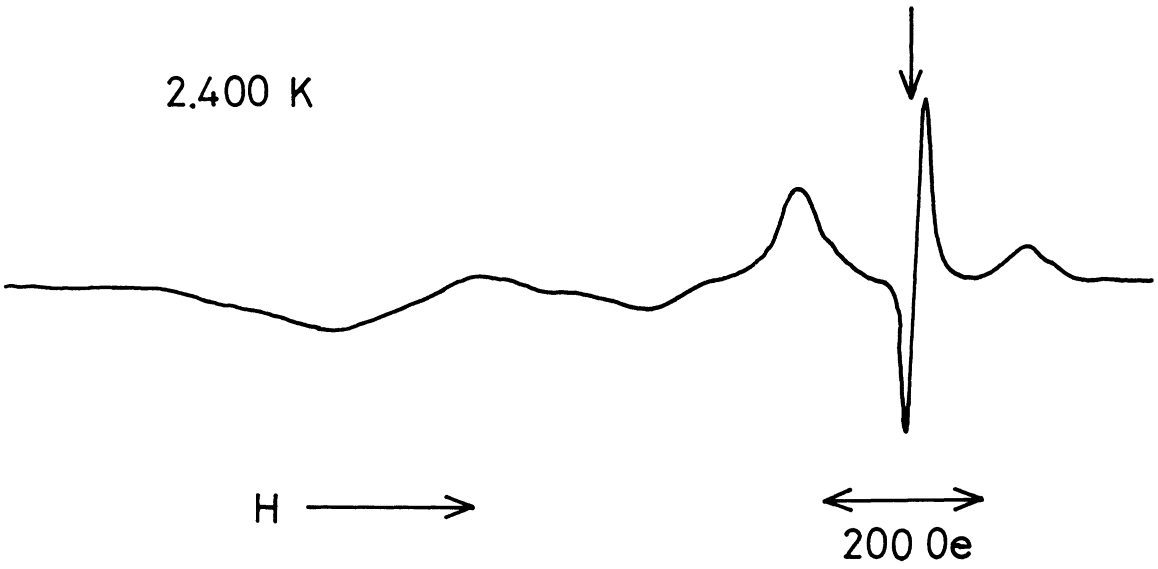

Fig. 3. Another antiferromagnetic resonance absorption of powdered p-Cl-BDPA.

the theory of antiferromagnetic resonance, the high field line is due to the case where the external field is applied parallel to the spin easy axis and is large enough to make spins flop perpendicular to the spin easy axis. This may imply the anisotropy field necessary for the spin axis to be fixed in the antiferromagnetic state is very small as compared with usual transition metal ion compounds. On the other hand, the two lines in the low field side are due to the cases where the external field is applied along the next easy axis and the hard axis respectively. This suggests that the anisotropic field has an orthorhombic symmetry. Detailed analyses are now in progress and will be published elsewhere.

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