The Mechanism of the Piezochromism of Hexaphenyl-biimidazolyl

By Taro HAYASHI and Koko MAEDA

(Received March 1, 1965)

We have found that 2,2',4,4',5,5'-hexaphenyl-1,1'-biimidazolyl and its derivatives, which exhibit both photochromism and thermochromism,[1] which have been ascribed to a radical dissociation of the N-N bond,[2] exhibit also piezochromism and that the mechanism of this is a radical dissociation of the N-N bond brought about mechanically on grinding or pressing. This piezochromism is probably the first case in which the mechanism has been elucidated.

When pale yellow fine crystals of hexaphenyl-biimidazolyl which had been recrystallized from benzene, m. p. 198—199°C, were ground in an agate mortar or pressed at a pressure of about 10—50 kg./cm^2 at room temperature in the dark, they turned reddish-purple. The reddish-purple crystals reverted to the original pale yellow crystals when kept at about 50°C in the dark or when subjected to liquid or to the vapor of ether, ethanol, acetone or benzene.

This piezochromism is not the thermochromism ascribed to a rise in temperature upon grinding or pressing, because the reddish-purple color due to the thermochromism began to appear at about 170°C, which was unlikely to occur upon grinding or pressing, and the piezochromic color hardly faded at room temperatures, whereas the thermochromic color disappeared immediately upon the crystals being cooled to room temperature. The pale yellow solid exhibited no ESR, whereas the reddish-purple solid obtained by grinding or pressing exhibited an ESR of a single peak (g=2.003), as in the cases of the photochromism and the thermochromism in a solid state. The spin concentration in the reddish-purple solid which has been obtained by grinding for 5 min. was about 10^{16}—10^{17} spins/g. This fact indicates the formation of a free radical on grinding or pressing.

The reddish-purple solid, obtained by grinding for 5 min. in the dark or by pressing at a pressure of 30 kg./cm^2 for 5 min. at room temperature, showed an absorption maximum at 563 mμ ; the maximum was measured by the

1) T. Hayashi and K. Maeda, This Bulletin, 33, 566 (1960).
2) T. Hayashi and K. Maeda, ibid., 37, 1564 (1964); 37, 1717 (1964).

opal-glass transmission method and the potassium bromide disk method respectively. A benzene solution of the reddish-purple solid showed an absorption maximum at 554 mμ, a value which agreed with the 554 mμ assigned to the triphenylimidazolyl produced in a benzene solution of hexaphenyl-biimidazolyl on irradiation.

These results indicate that the free radical produced in the piezochromism of hexaphenyl-biimidazolyl is triphenylimidazolyl and that the piezochromism of hexaphenyl-biimidazolyl may be ascribed to the dissociation of the N-N bond to triphenylimidazolyl which is mechanically brought about on grinding or pressing. It seems probable that this conclusion is correct, since the heat of the dissociation of hexaphenyl-biimidazolyl to triphenylimidazolyl by the homolytic rupture of the N-N bond, ΔH, was found to be 26 kcal./mol.[2] in a benzene solution.

2, 2', 4, 4', 5, 5'-Hexa-*p*-tolyl-1, 1'-biimidazolyl, fine, pale greenish-yellow crystals, m. p. 194—195°C, hexa-*p*-chlorophenyl-biimidazolyl, fine, yellow crystals, m. p. 213—214°C and 2, 2'-di-*p*-chlorophenyl-4, 4', 5, 5'-tetraphenyl-1, 1'-biimidazolyl, fine, almost colorless crystals, m. p. 219—220°C which exhibited[2] both photochromism and thermochromism in a solution and in the solid state, were found to exhibit the piezochromism, the color changing from pale greenish-yellow to pale bluish-violet (absorption maximum 589 mμ in the solid state), from yellow to pale bluish-violet (absorption maximum 586 mμ) and from colorless to pale violet (absorption maximum 578 mμ) respectively. The mechanism of the piezochromism in these cases was found to be the same as that of hexaphenyl-biimidazolyl.

The decay rate of ESR due to the piezochromism of hexaphenyl-biimidazolyl was measured by the decrease in the signal intensity h (the vertical distance betweeen two peaks of a signal[2]) and found to obey the following formula; $1/2(1/h^2-1/h_0^2)=kt$, which was obtained by the substitution of h for the concentration in the rate expression of the third order reaction. The values of k were 2.0×10^{-5} at 48.0°C and 8.9×10^{-5}(cm^{-2}, min^{-1}) at 51.5°C. Since the line widths of the signals were almost constant during the measurement, h can be assumed to be approximately proportinal to the concentration of triphenylimidazolyl. Hence, the rate of the recombination of triphenylimidazolyl in the fading process of the piezochromism appears to be of the third order, and hence different from the second order of the rate of the recombination of triphenylimidazolyl in the photochromism in a solution.[2] This result seems to suggest that the recombination of triphenylimidazolyl in the piezochromism takes place through a diffusion process which is the rate-determining step of the third order with respect to triphenylimidazolyl.

Department of Chemistry
Faculty of Science
Ochanomizu University
Otsuka, Bunkyo-ku, Tokyo