SHORT COMMUNICATIONS

Infrared Absorption Spectra of Photochromic and Piezochromic Systems of the Dimers of Triarylimidazolyls

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The compounds, such as $C_{42}H_{30}N_4$, (A) (m. p. 199—200°C), $C_{48}H_{42}N_4$ (B) (m. p. 194—195°C), $C_{42}H_{24}N_4Cl_6$ (C) (m. p. 213—214°C) and $C_{42}H_{28}N_4Cl_2$ (D) (m. p. 219—220°C), produced by the oxidation of corresponding 2, 4, 5-triarylimidazoles, have previously been found1) to exhibit photochromism, thermochromism and piezochromism. It was then determined that these compounds were the dimers of triarylimidazolyl radicals2,3) and that the colors exhibited by the

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1) T. Hayashi, K. Maeda, S. Shida and K. Nakada, *J. Chem. Phys.*, **32**, 1568 (1960).

2) T. Hayashi and K. Maeda, This Bulletin, **35**, 2057 (1962).

3) T. Hayashi, K. Maeda and M. Morinaga, ibid., **37**, 1563 (1964); T. Hayashi, K. Maeda and M. Takeuchi, ibid., **37**, 1717 (1964); T. Hayashi and K. Maeda, ibid., **38**, 685 (1965).

TABLE I. THE INFRARED ABSORPTION BANDS OF THE DIMERS OF TRIARYLIMIDAZOLYLS IN THE 1620—1480 cm^{-1} REGION (KBr pellet)

Compound	Wave number, cm^{-1}
A	1617 (sh), 1603 (s), 1577 (m), 1565 (m), 1554 (s), 1526 (sh), 1501 (m), 1485 (s)
B	1622 (sh), 1604 (s), 1574 (sh), 1568 (m), 1551 (sh), 1520 (w), 1501 (s)
C	1616 (sh), 1600 (s), 1572 (w), 1560 (sh), 1553 (m), 1519 (w), 1495 (sh), 1484 (s)
D	1618 (sh), 1604 (m), 1575 (w), 1565 (m), 1556 (m), 1525 (sh), 1501 (m), 1484 (s)

(s, strong; m, medium; w, weak; sh, shoulder)

TABLE II. THE INFRARED ABSORPTION BANDS CHARACTERISTIC OF TRIARYLIMIDAZOLYL RADICALS PRODUCED PHOTOCHROMICALLY OR PIEZOCHROMICALLY

Triarylimidazolyl	Wave number, cm^{-1}
2,4,5-triphenyl-	870 (sh)
2,4,5-tri-*p*-tolyl-	551, 881 (sh), 1359
2,4,5-tri-*p*-chlorophenyl-	882 (sh)
2-*p*-chlorophenyl-4,5-diphenyl-	610 (sh), 812, 877 (sh), 883 (sh), 1142

photochromism, thermochromism or piezochromism are due to the triarylimidazolyl radicals produced by the dissociation of the dimers by irradiation, heating or grinding respectively.³⁾

The infrared absorption spectra of the compounds mentioned above and of the photochromic and piezochromic systems (KBr pellet) have now been observed with a Perkin-Elmer 521 grating infrared spectrophotometer.

The absorption bands of the dimers of triarylimidazolyls in the 1620—1480cm^{-1} region are shown in Table I.

As was to be expected from the mechanism,³⁾ the spectra of the photochromic systems of these compounds were similar to those of the respective piezochromic systems. One or several new weak bands were observed in the spectra of the photochromically- and piezochromically-colored systems, as is shown in Table II.

Recently, White and Sonnenberg⁴⁾ showed that, in the 1620—1480 cm^{-1} region, aryl-2*H*-imdazoles exhibit the characteristic bands at approximately 1615(w) and 1550 cm^{-1}(m–s), while arylimidazoles do not exhibit such bands and tetraphenyl-4*H*-imidazole exhibits strong bands at 1594 and 1563 cm^{-1}, along with the 1616 cm^{-1} band. Since in the 1620—1480 cm^{-1} region the absorption bands of the dimers of triarylimidazolyls were very similar to the characteristic bands of the aryl-2*H*-imidazoles, as is shown in Table I, the results may suggest that the structures of the dimers of triarylimidazolyls are not the hexaaryl-*N*, *N'*-biimidazolyls which were previously reported,³⁾ but rather hexaaryl-2, 2'-bi-2*H*-imidazolyls produced by the dimerization of the 2, 4, 5-triarylimidazolyl radicals at the 2-position, and that the homolytic dissociation of the C–C bond of hexaaryl-2, 2'-bi-2*H*-imidazolyls into 2, 4, 5-triarylimidazolyl radicals is the more probable mechanism of the photochromism, thermochromism and piezochromism of the dimers of triarylimidazolyls than the dissociation of the N–N bond of hexaaryl-*N*, *N'*-biimidazolyls. In order to determine more exactly the constitution of the dimers and the mechanism of the photochromism, thermochromism and piezochromism, further investigations are now being carried out.

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4) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).