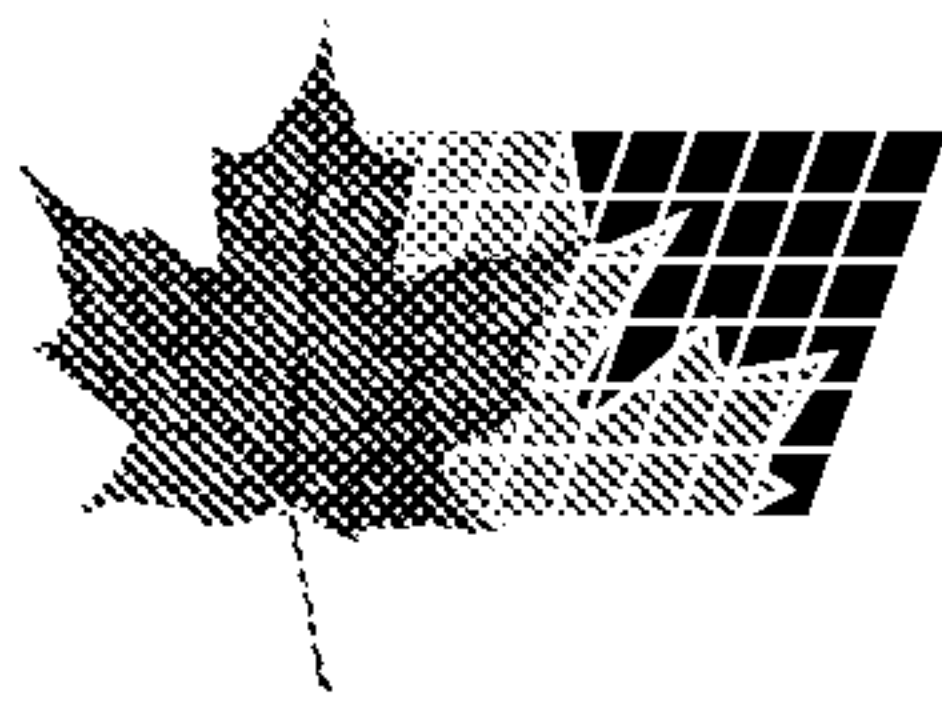




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(54) **FILTRE OPTIQUE AFFAIBLISSEUR DE FAISCEAUX LASER**

(54) **LASER-ATTENUATIVE OPTICAL FILTER**

(57) An optical filter for absorbing neodymium YAG-doubled laser radiation at 532 nanometers, comprising a polymeric matrix of transparent polycarbonate containing platinum deuteroporphyrin IX dimethyl ester, has an optical density of 1.8 at 532 nm while having a photopic luminous visible transmission of 53.8%. Optionally, the filter may contain other additives for absorption at other laser wavelengths, such as vanadyl tetra-4-tert-butylphthalocyanine for absorption of ruby laser radiation at 694 nanometers and tris(p-diethylaminophenyl) aminium hexafluoroantimonate for absorption of neodymium YAG laser radiation at 1064 nanometers.



Abstract of the Disclosure

5 An optical filter for absorbing neodymium YAG-dou-
bled laser radiation at 532 nanometers, comprising a polymeric
matrix of transparent polycarbonate containing platinum deu-
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10 vanadyl tetra-4-~~tert~~-butylphthalocyanine for absorption of
ruby laser radiation at 694 nanometers and tris(p-diethylami-
nophenyl)aminium hexafluoroantimonate for absorption of neo-
dymium YAG laser radiation at 1064 nanometers.

Title of the Invention

LASER-ATTENUATIVE OPTICAL FILTER

Background of the Invention

5 This invention relates to an optical filter for attenuating incident laser radiation and, more particularly, to a filter for absorbing neodymium YAG-doubled laser radiation at 532 nanometers (nm).

10 In certain applications, it is necessary to attenuate incident laser radiation at one or more laser wavelengths, while at the same time transmitting a substantial portion of the incoming radiation at other wavelengths. One such application involves visors worn by military personnel. Because of the extremely high intensity of the laser radiation, the attenuation at laser wavelengths must be correspondingly high: optical densities of 3 or more at the laser wavelength are
15 typical for filters of this type. In order to satisfy these twin requirements of high attenuation at the laser wavelength and substantial transmission at adjacent wavelengths, the filter must have an extremely sharp cutoff characteristic.

20 Optical filters are commonly made by incorporating one or more compounds, selected for their absorption characteristics, into a suitable light-transmissive host material--in particular, a polymeric matrix such as polycarbonate. To be useful for such an application, the absorber must have several properties besides absorption at the desired wave-
25 length. The compound should be soluble in the host material, and should be compatible with the host material and any other additives. The compound should be sufficiently stable to permit its incorporation and use in the desired host material

without excessive degradation. Finally, the compound should be capable of being readily synthesized on the scale desired.

McKoy et al U.S. Patent No. 4,622,174 discloses a transparent protective laser shield containing metalloporphyrins--more particularly, platinum octaethylporphyrin (PtOEP) for absorption of neodymium YAG-doubled laser radiation at 532 nm and vanadyl phthalocyanine (VOPc) for absorption of ruby laser radiation at 694 nm. Gordon U.S. Patent No. 4,657,345 discloses a similar shield in which the absorbers are diffused into a surface of the host material rather than being disseminated uniformly through it. Although PtOEP absorbs strongly at 532 nm, its absorption maximum does not coincide with that wavelength, but occurs at a slightly longer wavelength, at about 537 nm. Because of the extreme sharpness of the absorption peak, this implies that more of the absorber must be used to achieve a given optical density at the laser wavelength than if the absorption maximum coincided with the laser wavelength. Not only is the absorber relatively expensive, because of the platinum used, but the resulting filter will have a lower transmittance at other wavelengths because of the greater amount of material used.

Summary of the Invention

One object of our invention is to provide an optical filter that absorbs strongly at 532 nm.

Another object of our invention is to provide an optical filter that transmits a substantial amount of radiation at other wavelengths.

A further object of our invention is to provide an optical filter which may include other additives for absorp-

tion at other wavelengths.

Still another object of our invention is to provide an optical filter that is simple and inexpensive to manufacture.

Accordingly, there is provided an optical device for absorbing radiation from a double neodymium YAG laser characterized in a notch filter having a sharp cutoff characteristic and providing selective high absorption of radiation at 532 nanometers wavelength and a second filter capable of selective high absorption of radiation at 1064 nanometers wavelength.

In general, our invention contemplates an optical filter comprising a light-transmissive, preferably transparent polymeric matrix containing the compound known formally as dimethyl 3,7,12,17-tetramethyl-21H,23H-porphine-2,18-dipropionate platinum (II), and more informally as platinum deuteroporphyrin IX dimethyl ester, or PtDPIXDME. This compound, the preparation of which is described in Milgrom, Polyhedron, 4, 1661 (1985), has an absorption maximum of 533 nm in polycarbonate, almost exactly coincident with the laser emission wavelength of 532 nm. As a result, less of the compound than, say, PtOEP is required to achieve a given

optical density at 532 nm. Not only is less platinum thus required as a starting material, but the filter transmittance at adjacent wavelengths is higher.

10 In use, the deuteroporphyrin compound may be incorporated into matrices or films of suitable light-transmissive, preferably transparent materials such as polycarbonate; acrylic polymers such as poly(methyl methacrylate); vinyl polymers such as poly(vinyl chloride); poly(allyl diglycol carbonate); and cellulose derivatives, preferably esters such as cellulose acetate, cellulose propionate, cellulose butyrate and the like, by such known methods as molding, extruding and casting to make solid sheets, plates, lenses, visors and the like.

The amount of absorber used in the host material is determined by the thickness of the host material and the optical density desired at the laser wavelength in accordance

with the Beer-Lambert law:

$$A = OD = -\log T/T_0 = \alpha bc$$

where A is the absorbance, or optical density (OD), due to the presence of the absorber at a specific wavelength; T is the transmittance of the filter at that wavelength with the absorber present; T_0 is the transmittance of the filter at that wavelength with the absorber absent; α is the mass absorption coefficient of the absorber in the host material at that wavelength ($L/(g \cdot cm)$); b is the path length through the host material (cm); and c is the mass concentration of the absorber in the host material (g/L). Equivalently, the Beer-Lambert law may be expressed as

$$A = \epsilon bc_m$$

where A and b are defined as before; ϵ is the molar extinction coefficient of the absorber in the host material at the wavelength in question ($L/(mol \cdot cm)$); and c_m is the molar concentration of the absorber in the host material (mol/L). Preferably, the host material should contain a sufficient amount of the absorber to have an optical density of at least about 2 at the laser wavelength. More preferably still, the filter should have an optical density of 3 or more at the laser wavelength.

The compound may also be used along with other additive such as dyes, infrared absorbers, ultraviolet absorbers, and stabilizers that do not adversely affect the compound or its absorptive properties. In particular, the deuteroporphyrin compound may be combined with a vanadyl phthalocyanine (VOPc) such as unsubstituted VOPc or, preferably, a more

soluble substituted VOPc such as vanadyl tetra-4-tert-butylphthalocyanine for additional absorption at 694 nm. The compound may also be combined with a tris(p-dialkylaminophenyl)aminium salt, especially tris(p-diethylaminophenyl)aminium hexafluoroantimonate, for absorption at the neodymium laser wavelength of 1064 nm. If the latter compound is used with poly(allyl diglycol carbonate), it should preferably be introduced into the matrix after polymerization, as by dyeing, to avoid undesirable interactions.

The deuteroporphyrin compound may be prepared from its unmetallated precursor, deuteroporphyrin IX dimethyl ester, in the manner described in Milgrom, Polyhedron, 4, 1661 (1985). Vanadyl tetra-4-tert-butylphthalocyanine, if used as another additive for absorption at 694 nm, may be prepared from 4-tert-butylphthalonitrile and vanadium trichloride in the manner described in Law, Inorg. Chem., 24, 1778 (1985). Alternatively, the vanadyl compound may be prepared from 4-tert-butylphthalic acid and vanadyl sulfate.

Milionis et al U.S. Patent No. 3,400,156 describes the preparation of tris(p-dialkylaminophenyl)aminium salts and their incorporation into plastics as infrared absorbers. Susi et al U.S. Patent No. 3,341,464 specifically describes the preparation and use of tris(p-dialkylaminophenyl)aminium hexafluoroarsenates and hexafluoroantimonates.

Brief Description of the Drawings

In the accompanying drawings to which reference is made in the instant specification and which are to be read in conjunction therewith and in which like reference numerals are used to indicate like parts in the various views:

FIGURE 1 shows the structural formula of the compound platinum deuteroporphyrin IX dimethyl ester.

FIGURE 2 shows the structural formula of the compound vanadyl tetra-4-tert-butylphthalocyanine.

FIGURE 3 is a graph of the absorption spectrum of the compound of FIGURE 1 in solution.

FIGURE 4 is a graph of the transmission spectrum of an optical filter containing the compound of FIGURE 1.

Description of the Preferred Embodiments

EXAMPLE 1

Platinum deuteroporphyrin IX dimethyl ester (FIGURE 1), was prepared in the manner described in Milgrom, Polyhedron, 4, 1661 (1985). 2.7 mg of the compound were dissolved in 100 mL of pyridine and placed in an absorption cell of 1 cm thickness. The extinction coefficient ϵ observed at 533.5 nm was 41,000 L/(mol·cm). The absorption spectrum of the compound in pyridine solution is shown in FIGURE 3. Absorption maxima were observed at 533.5 nm ($A = 1.488$), 500.5 nm (0.479) and 384.0 nm (2.482). Absorption minima were observed at 649.5 nm (0.019), 513.0 nm (0.276) and 465.5 nm (0.164).

EXAMPLE 2

0.194 g of the porphyrin of Example 1 was mixed with 500 g of polycarbonate by placing the two materials in a blender for 1 minute. The mixture was dried at 250°F for 1½ hours, and then injection molded to produce a disk 0.038 inch thick. The injection pressure alternated between a high of 1800 psi and a low of 1500 psi. The clamp pressure was 2100 psi, and cycle time 17.7 seconds. The nozzle temperature was

458°F, the front zone of the barrel was 450°F, and the rear zone of the barrel was 430°F.

The disk showed an intense absorption at 532 nm (OD = 1.8), with high transmission of light at other wavelengths in the visible region. The transmission spectrum of the disk is shown in FIGURE 4. The disk serves as a "single-notch" laser filter at 532 nm while exhibiting high visible-light transmission. The photopic luminous transmission (Illuminant C) was 53.8 %.

EXAMPLE 3

To the mixture of Example 2 is introduced 0.0165 g of vanadyl tetra-4-tert-butylphthalocyanine (FIGURE 2). The mixture was injection molded to produce a plate 0.110 inch thick. The plate exhibited an optical density of 3.4 at 532 nm and 1.5 at 694.3 nm (the ruby laser wavelength), with a photopic luminous transmission of 27.9%. The part serves as a highly light-transmissive laser filter which simultaneously filters laser radiation at 532 nm and 694.3 nm.

EXAMPLE 4

To the mixture of Example 2 is introduced 0.526 g of tris(p-diethylaminophenyl)aminium hexafluoroantimonate (U.S. Patent No. 3,341,464). This mixture was injection molded to produce a plate 0.073 inch thick which exhibited optical densities of 2.7 at 532 nm and 2.8 at 1064 nm (neodymium YAG laser wavelength). The part serves as a highly light-transmissive laser filter which simultaneously filters laser radiation at the two noted wavelengths.

It will be seen that we have accomplished the ob-

jects of our invention. Our optical filter absorbs strongly at 532 nm, while at the same time having a high transmittance at adjacent wavelengths in the visible region. The light-absorbing compound of our filter is capable of incorporation in a plastic polymeric matrix, and may be used with other additives such as light absorbers.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and combinations. This is contemplated by and within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, what we claim is:

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An optical device for absorbing radiation from a double neodymium YAG laser characterized in

first notch filtering means having a sharp cutoff characteristic and comprising a porphyrin dye for providing selective high absorption of radiation at 532 nanometers wavelength and

second filtering means comprising an infrared absorbing dye for providing selective high absorption of radiation at 1064 nanometers wavelength.

2. A device as in Claim 1 further including a light-transmissive polymeric matrix containing the first and second filtering means.

3. A device as in Claim 1 in which the second filtering means comprises a tris (p-dialkylaminophenyl) aminium salt.

4. A device as in Claim 1 in which the second filtering means comprises a tris (p-diethylaminophenyl) aminium hexafluoroantimonate.

5. A device as in Claim 1 wherein the porphyrin dye is selected from the group consisting of platinum octaethylporphyrin and platinum deuteroporphyrin dimethyl ester.

6. A device as in Claim 1 further including a third filtering means providing selective high absorption of radiation at 694 nanometers wavelength.

7. A device as in Claim 6 in which the third filtering means comprises a vanadyl phthalocyanine.

8. A device as in Claim 6 in which the third filtering means comprises vanadyl tetra-4-tert-butylphthalocyanine.

9. A device as in Claim 6 further including a light-transmissive polymeric matrix containing the first and second and third filtering means.

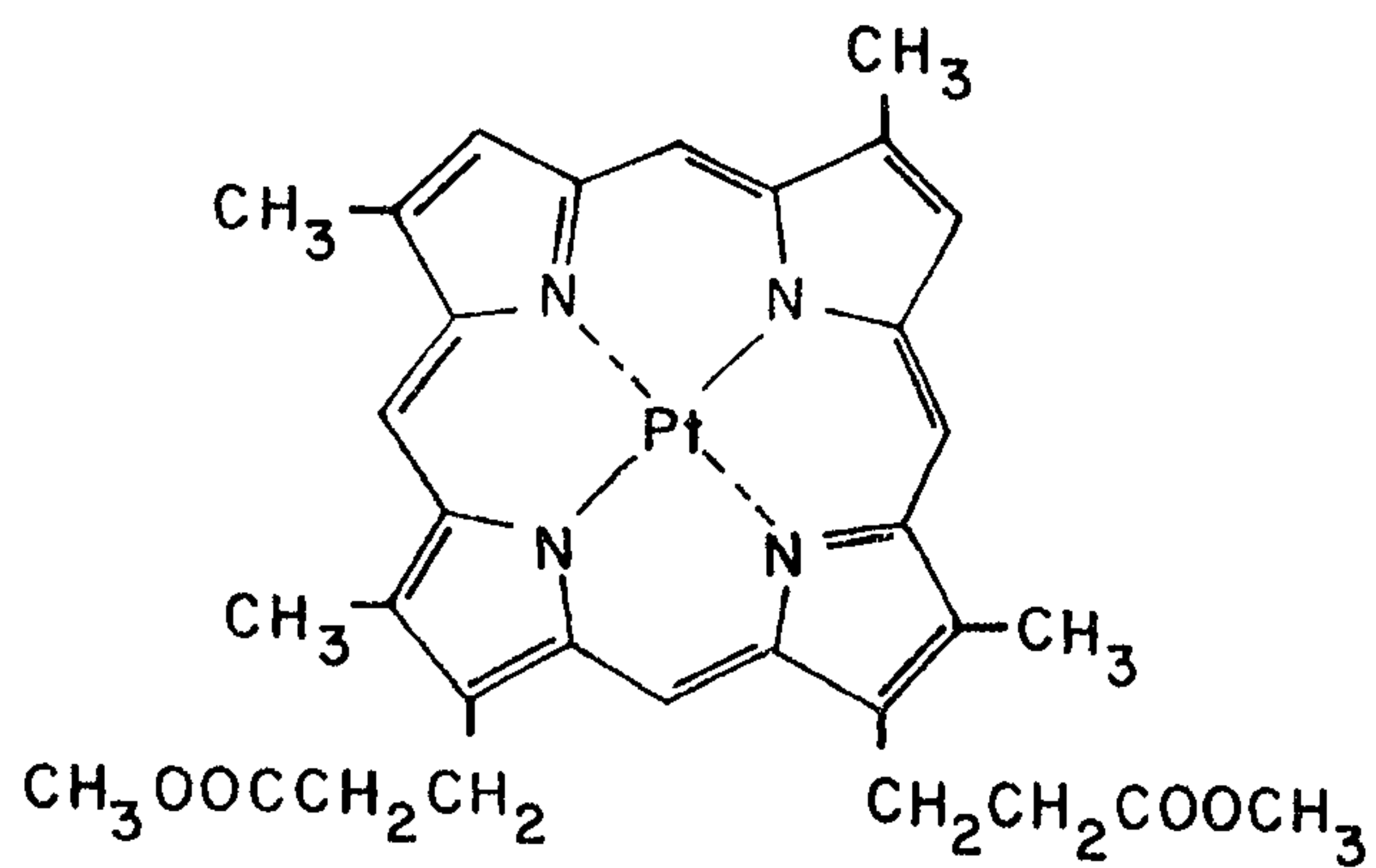


FIG. 1

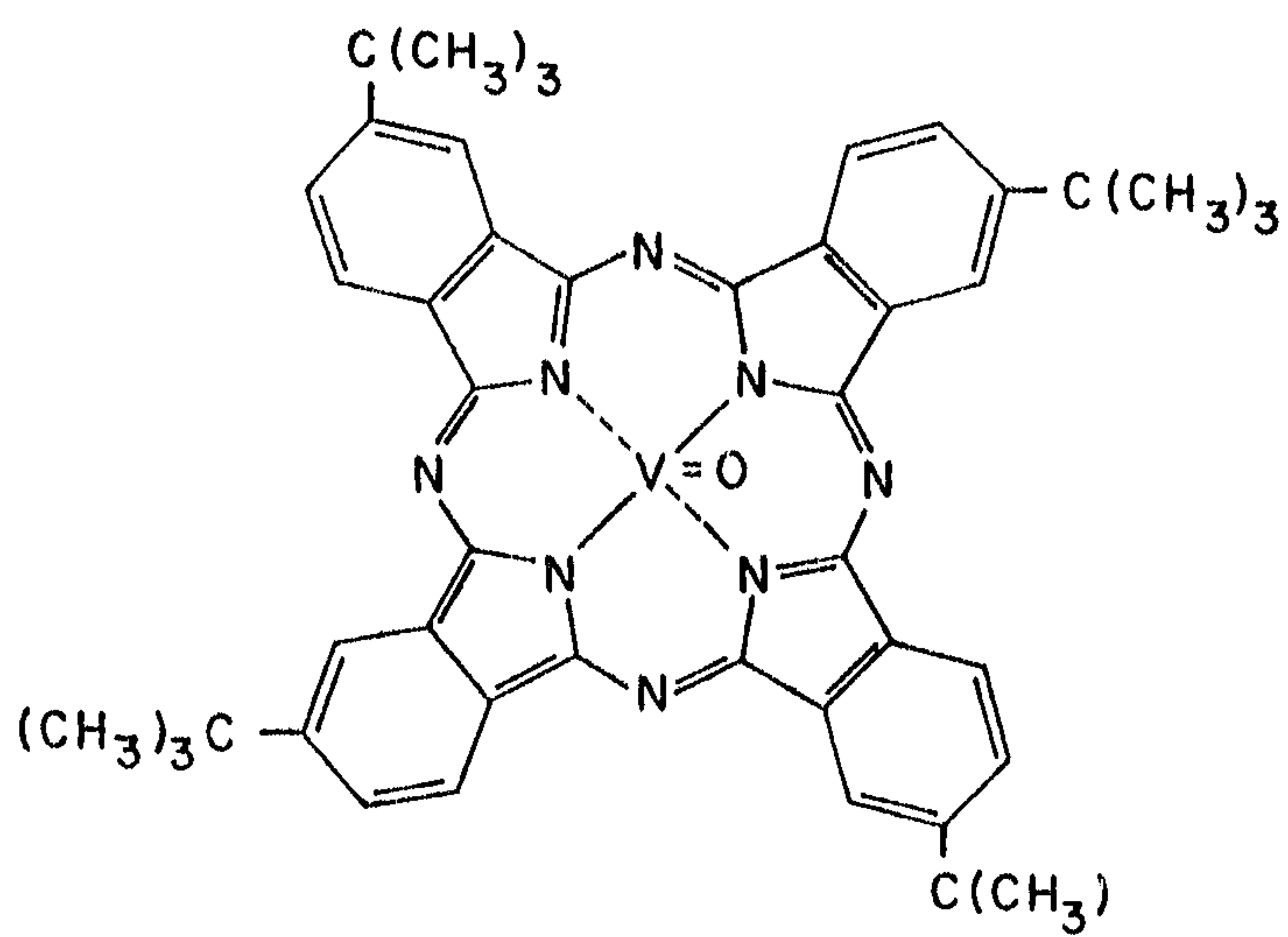


FIG. 2

FIG. 3

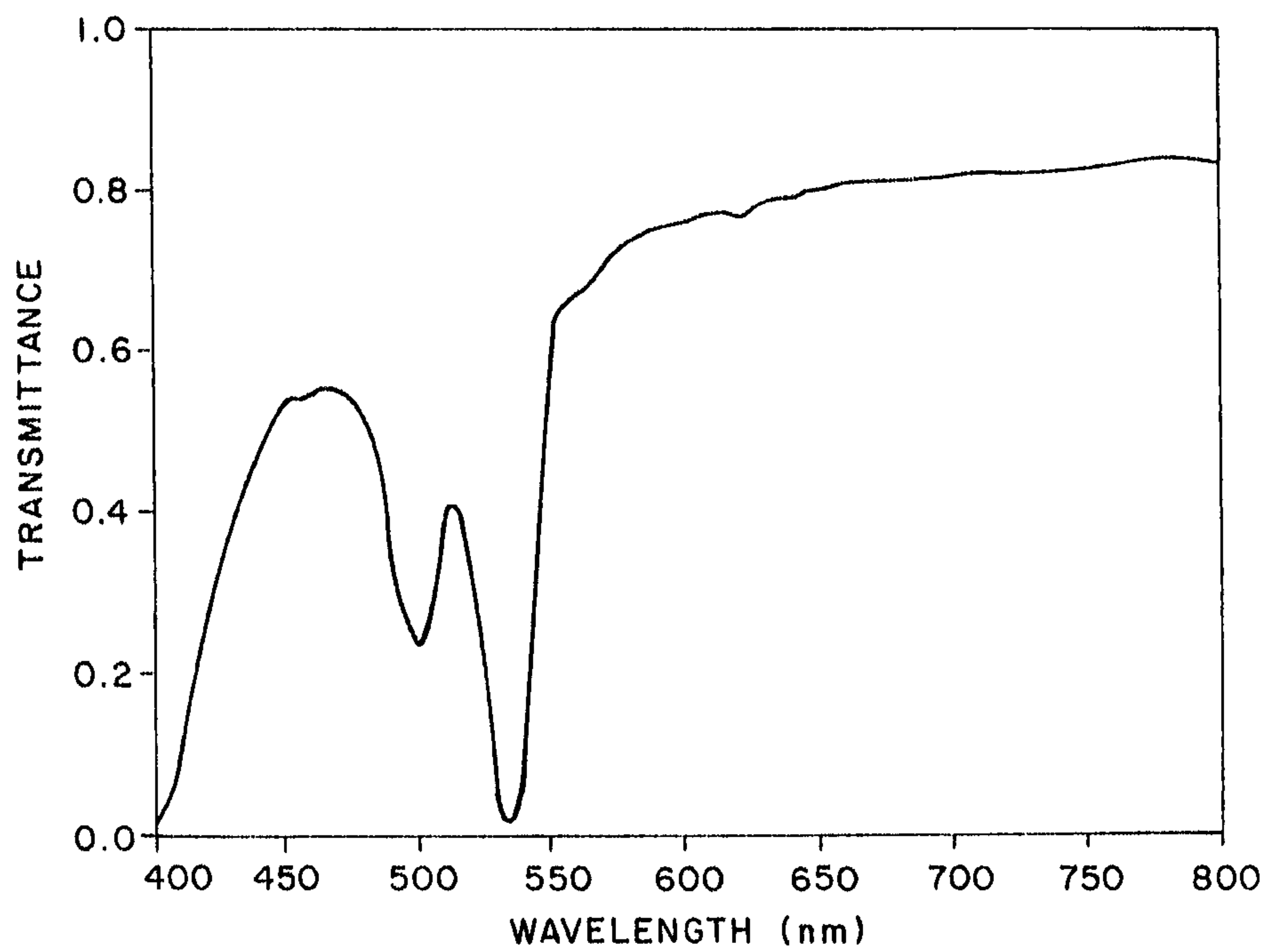
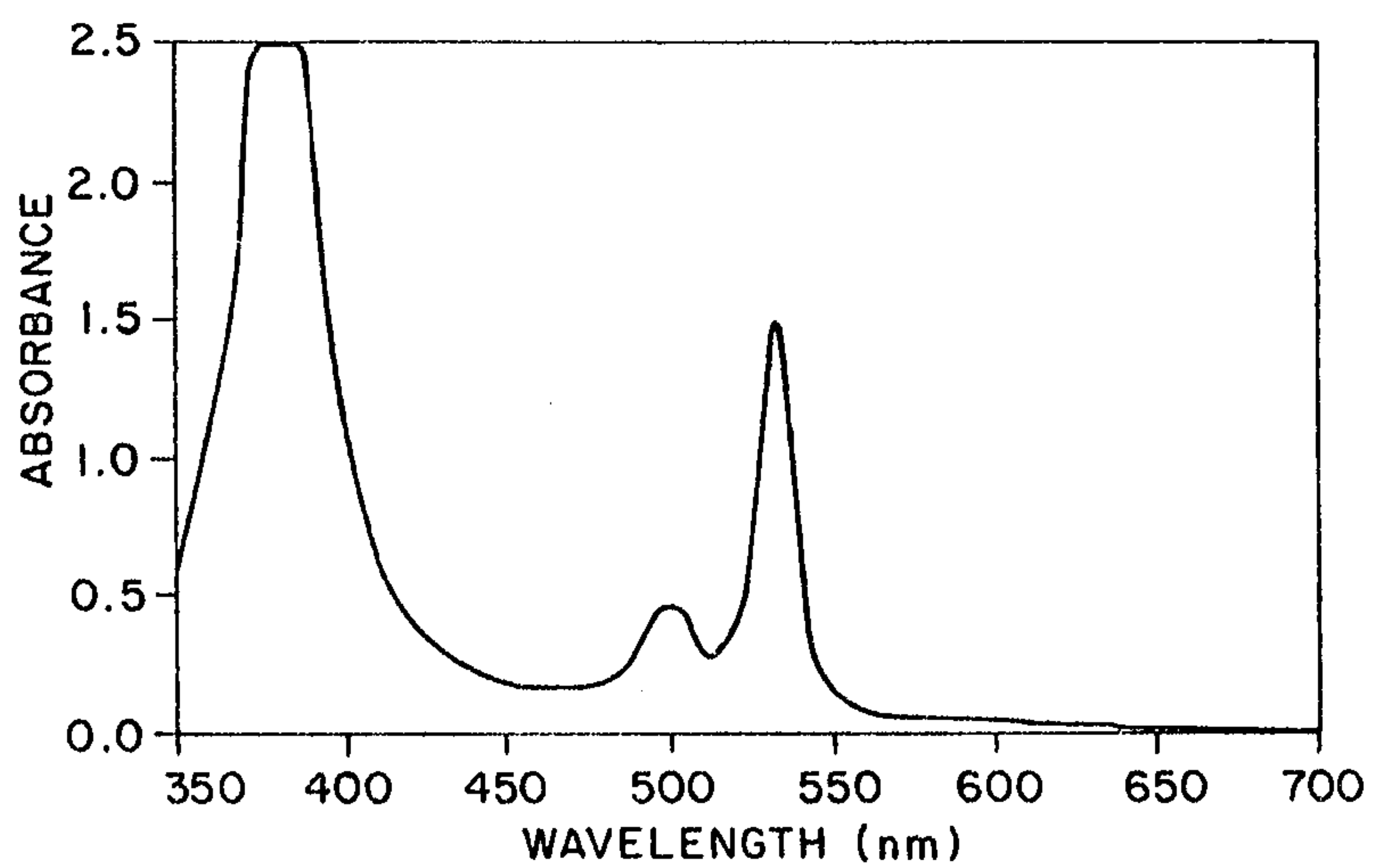


FIG. 4