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Deuterated Derivatives of 3,5-Dimethyl-1-(4-nitrophenyl)pyrazole for Nonlinear Optical Materials

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A weak absorption of laser light by a nonlinear optical crystal causes a noticeable temperature rise in the crystal. Such absorption may undesirably shift the reflactive indices (some optical characteristics) of the crystal. 3,5-dimethyl-1-(4-nitrophenyl)pyrazole [DMNP], an excellent nonlinear optical material, was deuterated in order to suppress its absorption in the 1 μm wavelength region.

Three deuterated deriatives were synthesized; their crystal structures were identical with that of DMNP. The deuteration of the pyrazole part including the two methyl moieties proved to be more effective than deuteration of the phenyl part (benzene ring) with regard to a reduction of the IR absorption.

A good correlation was confirmed between the temperature elevation under laser irradiation and IR absorption.

Blue-light second-harmonic generation (SHG) devices are one of the desirable light sources used for the high memory density writing of optical-disk. 3,5-Dimethyl-1-(4-nitrophenyl)pyrazole [DMNP] is known to be an excellent nonlinear optical (NLO) compound that is suitable for blue-light SHG devices.[1—3] Y. Okazaki et al. reported that DMNP shows phase-matching properties at 1064 nm[3] and A. Harada et al. reported that DMNP generates blue light in a cored fiber structure.[4]

One problem concerning the DMNP crystal is temperature elevation when irradiated with a 900—1100 nm laser beam, which is the fundamental waves for blue and green second-harmonic light. This temperature elevation, probably caused by a weak absorption of the laser energy in the NIR region due to the vibration of C–H bonds in the DMNP molecule, may change the refractive indices (or other optical characteristics of the crystal) and thus cause some chemical changes in the crystal. With the aim of making DMNP more robust as an optical element, deuterated derivatives of DMNP were synthesized and their NIR and IR spectra as well as temperature elevation with laser irradiation were analyzed.

Results and Discussion

Figure 1 shows the vis-NIR spectrum of a DMNP single crystal, which has absorption bands in the 1100—1200 nm (slightly lower in energy than the triple overtones of the C–H stretching vibration bands), 1300—1500 nm and 1600—1750 nm (corresponding to double overtones) regions. However, no absorption bands have been observed between 900 and 1100 nm, though radiation with a laser of this wavelength region elevated the temperature of the DMNP crystal. Through a series of more careful spectroscopic as well as temperature measurements, very weak absorption bands were observed in the region of concern, as shown in Fig. 2. In this experiment the DMNP crystal used was of the best quality, selected from many samples and carefully polished. Then a Ti–Sapphire laser, which is a wavelength-variable laser, was employed for temperature measurements. Although these two weak bands (1009 and 1058 nm) are fairly higher in energy than the triple overtones of the C–H stretching vibration bands, the authors presumed that they are related to C–H vibrations and that these absorptions may be reduced by the deuteration of DMNP.

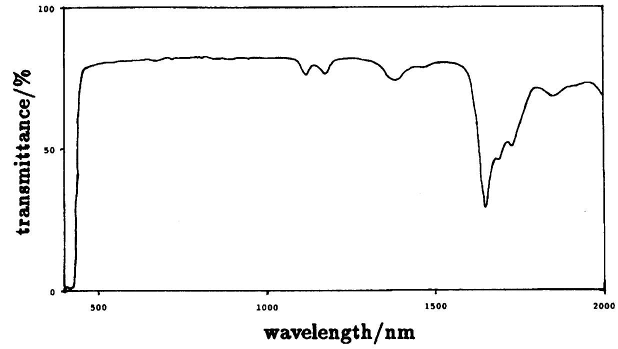


Fig. 1. Vis-NIR spectrum of a DMNP single crystal.

Three derivatives of DMNP (**D4**, **D7**, and **D11**) were synthesized by the reaction of 2,4-pentanedione with 4-nitrophenylhydrazine according to Scheme 1. Deuterated positions of the derivatives were confirmed by the ^{1}H NMR spectra. The deuterated ratio of the methyl, 4-position of pyrazole, and the phenyl of the derivatives were 91%. 95%, and almost 100%, respectively. The IR spectra of these derivatives are shown in Figs. 3, 4, and 5 and that of DMNP is shown in Fig. 6.

These spectra clearly indicate the dependence of absorbance reduction for the C–H stretching bands on the deuterated positions (2800—3050 cm^{-1} for C(sp^3)–H and 3050—3200 cm^{-1} for C(sp^2)–H).

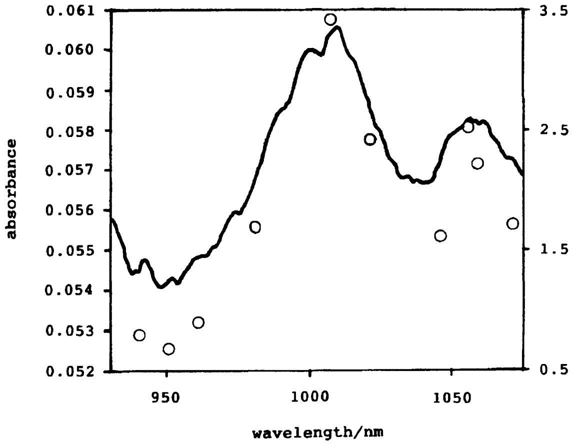
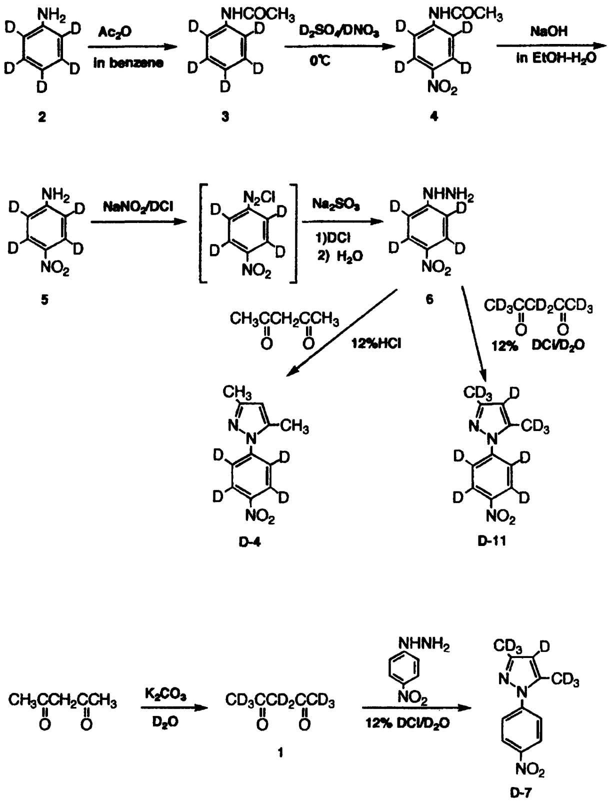


Fig. 2. NIR spectrum (solid line) and temperature elevation (open circles) of a DMNP single crystal.



Scheme 1.

The vis-NIR spectra of the deuterated derivatives in the single-crystalline state are shown in Figs. 7, 8, and 9. These spectra indicate a rule in absorbance reduction in the 1100—1200 nm bands and the 1600—1750 nm bands; deuteration of the methyl group can effectively reduce the absorbance in the longer wavelength parts of two bands, while, in contrast, deuteration of the phenyl group affects the shorter wavelength parts.

With reference to Figs. 3, 4, and 5, it is evident that these effects accurately correspond to those on the fundamental C–H stretching bands, indicating that the 1100—1200 nm bands are associated with the triple overtone of the C–H stretching bands and the 1600—1750 nm bands with a double overtone.

Regarding the weaker absorption bands in the 900—1100 nm region, a spectroscopic measurement did not provide us with precise information, mainly due to the insufficient quality of the crystals because of insufficient quantities of deuterated samples.

Instead of a spectroscopic measurement, the authors decided to measure the temperature elevation of the crystal under laser irradiation since a proportional relationship between the absorbance and the degree of the temperature rise has been confirmed with a polyacrylonitrile plate (Table 1) as well as with a polished DMNP single crystal (Fig. 2).

The temperature elevations of bulk crystals of DMNP and its deuterated derivatives under laser irradiation were examined at 1000 nm using a Ti–Sapphire laser. The results, expressed in terms of temperature elevation (°C) per watt, were as follows: DMNP 6.7, **D4** 5.8, **D7** 2.2, and **D11** 1.6. This indicates that deuteration of the pyrazole part including the two methyl groups suppresses a temperature elevation more effectively than does deuteration of the phenyl part. The results would

Table 1. Temperature Elevation of a Polyacrylonitrile Plate under Laser Irradiation[a)]

Absorption coefficient $\alpha/10^{-2}$ cm^{-1}	λ nm	ΔT °C
0.8	943	0.7
2.6	947	1.9
5.7	1004	5.0

a) The laser power was 0.7 W.

Table 2. Crystallographic Data of DMNP and the Deuterated Derivatives

	DMNP	**D4**	**D7**	**D11**
Crystal system	Orthorhombic			
Space group	$Pca2_1$			
Cell constants a/Å	21.383	21.369	21.386	21.359
b/Å	3.961	3.961	3.964	3.959
c/Å	12.604	12.579	12.587	12.569
V/Å^3	1067.5	1064.7	1066.9	1062.7

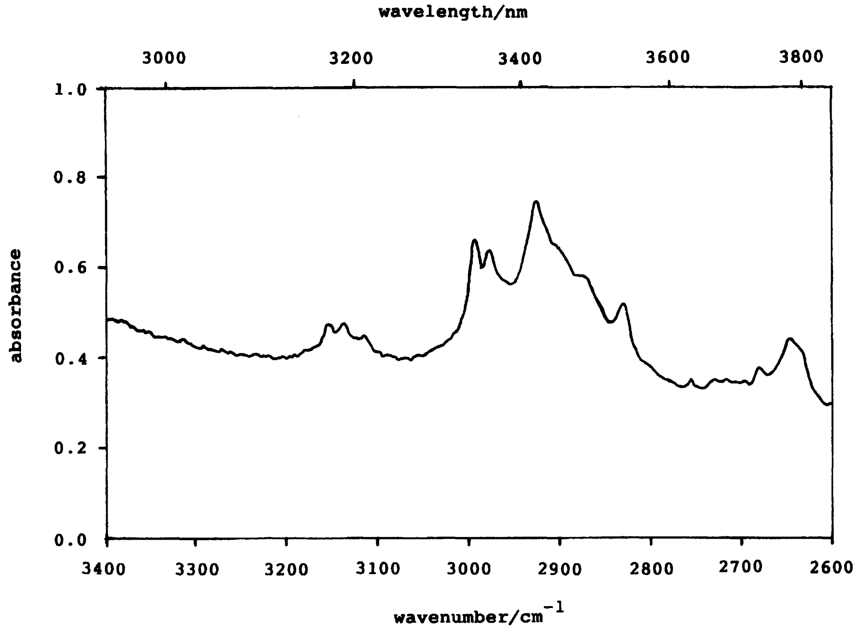


Fig. 3. IR spectrum of **D4**.

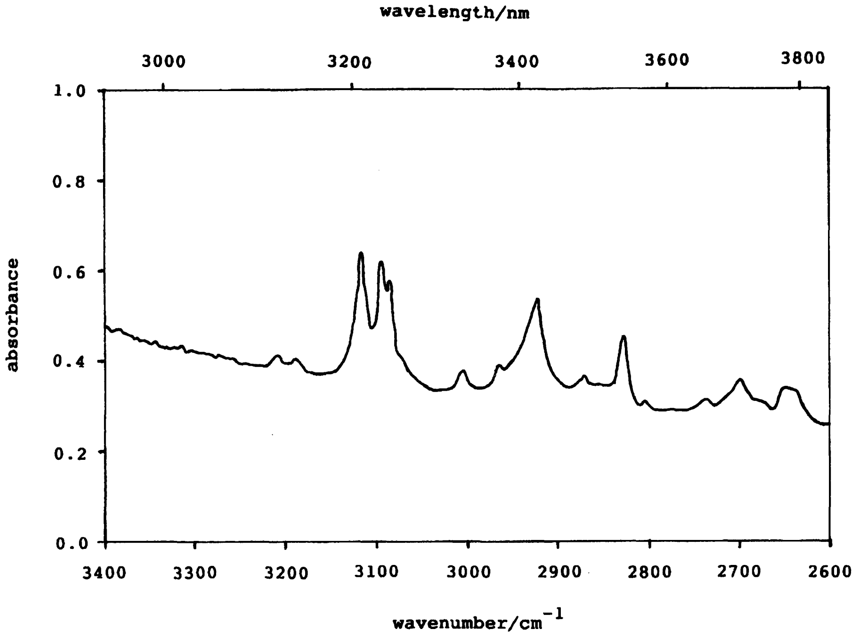


Fig. 4. IR spectrum of **D7**.

also indicate a decrease in light absorption at 1000 nm. It is evident that the preferable behavior of the **D7** and **D11** results from a decrease in light absorption at 1000 nm. The fact that the replacement of hydrogen for deuterium reduced the absorption at 1000 nm suggests that absorption is associated with C–H vibration. One possibility may be a combination of the triple overtone of C–H stretching vibration with C–H bending vibration. Also, the origin of two weak bands at around 1009 and 1058 nm (Fig. 2) may be understood in same the way.

The nonlinear optical properties of deuterated derivatives were examined by a powder SHG method. The results (vs. urea) were obtained to be as follows: **D4** 16, **D7** 16, **D11** 14, and DMNP 16. The crystal structure is one of the important factors used to determine the nonlinear optical properties, and offers a more quantitative understanding than does the powder SHG method. The results of crystallographic X-ray analyses of undeuterated DMNP and the deuterated derivatives are summarized in Table 2, showing that all of the crystals belong to the same crystallographic system with substantially the same cell constants. It is thus evident that deuteration does not affect the nonlinear optical properties at all.

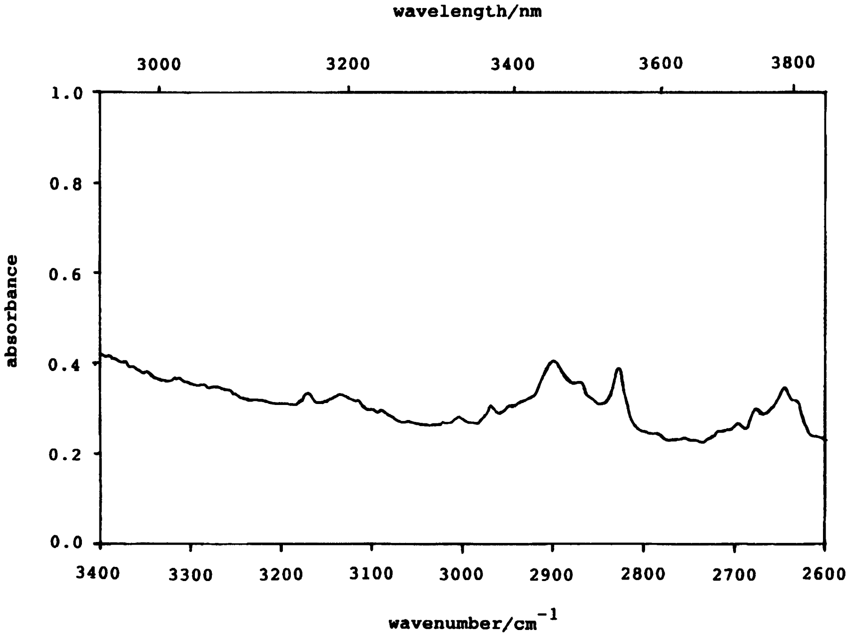


Fig. 5. IR spectrum of **D11**.

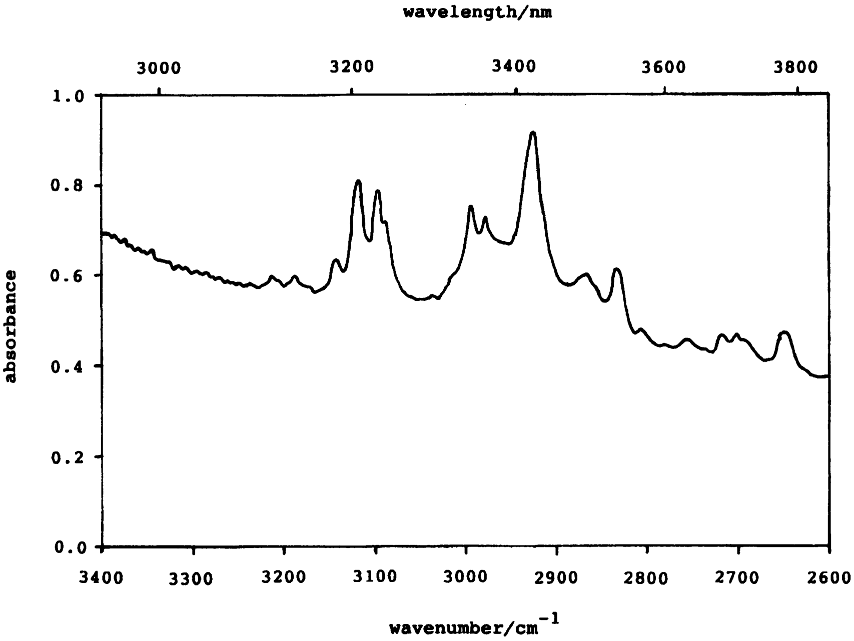


Fig. 6. IR spectrum of DMNP.

Conclusion

A weak absorption of the DMNP crystal at around 1000 nm elevates the temperature of the crystal under laser irradiation.

Even weakly absorbed laser energy by the DMNP crystal in the 1000 nm wavelength region noticeably elevates the temperature of the crystal. Deuteration of DMNP was found to effectively suppress such a temperature elevation. It is consequently concluded that the weak absorption at around 1000 nm is related to C–H stretching vibration. An X-ray crystallographic analysis of the deuterated crystals proved that deuteration did not affect the crystal structure at all. Thus, deuterated derivatives of DMNP show not only excellent nonlinear optical properties identical to DMNP, but also an improved durability for laser irradiation compared to DMNP.

Experimental

Synthesis. 2,4-pentanedione-d_8 (**1**) was synthesized by Egan's method.[5]

Synthesis of Acetanilide-2,3,4,5,6-d_5 (3): Acetic anhydride (52.0 g (0.51 mol)) was added dropwise to a mixture of aniline-2,3,4,5,6-d_5 (**2**) (deuterated more than 99%, purchased from Aldrich) (50.0 g (0.51 mol)) and 100

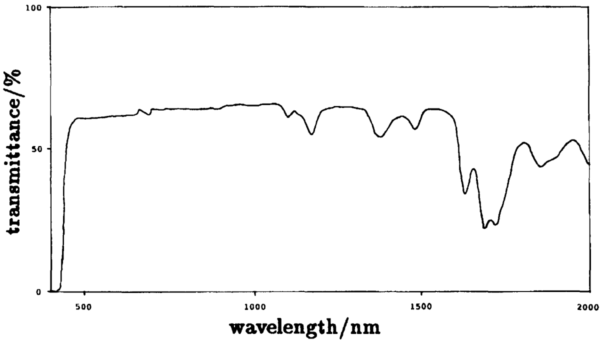


Fig. 7. Vis-NIR spectrum of a **D4** single crystal.

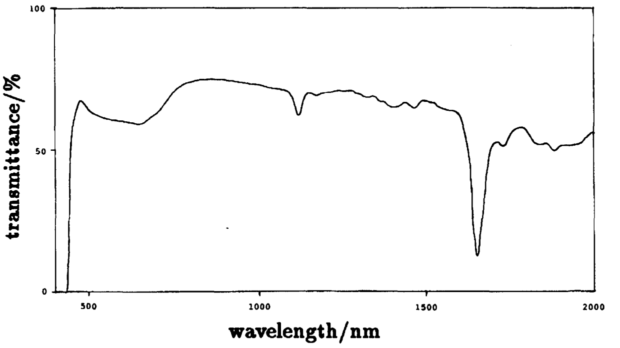


Fig. 8. Vis-NIR spectrum of a **D7** single crystal. Origin of the absorption of 500—700 nm is not obvious. It may be due to quality of the crystal.

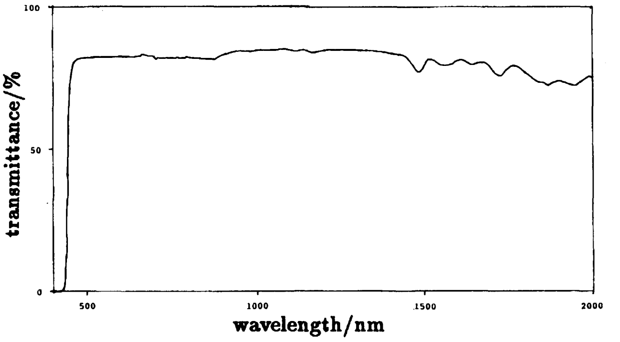


Fig. 9. Vis-NIR spectrum of a **D11** single crystal.

ml of anhydrous benzene so as to keep gentle refluxing under stirring. After the addition the reaction mixture was cooled by water and generated crystals were collected by filtration. The crystals were washed with by hexane, then dried in vacuum. Yield: 67.0 g (94.1%).

Synthesis of 4-Nitroacetanilide-2,3,5,6-d_4 (4): To a solution of 68% DNO_3 in D_2O 125 ml was added 98% D_2SO_4 150 g under cooling by an ice bath. To the resulting solution was added 67.0 g (0.48 mol) of **3** below 0 °C under stirring. The resulting mixture was then stirred at −10 to 5 °C for 6 h. and left standing overnight at room temperature. The resulting mixture was poured on crushed ice, the produced crystals were isolated by filtration. Yield: 62.0 g (70.4%).

Synthesis of 4-Nitroaniline-2,3,5,6-d_4(5): To a solution of NaOH (31.2 g (0.78 mol)), H_2O (90 ml) and ethanol (520 ml) was slowly added 34.5 g (0.24 mol) of **4**, the mixture was then refluxed for 1 h. To the resulting mixture was added H_2O (400 ml) dropwise under stirring. The resulting crystals were isolated by filtration and recrystallized from ethanol. Yield: 34.6 g (71.7%).

Synthesis of 4-Nitrophenyl-2,3,5,6-d_4-hydrazine (6): To a solution of 34.5 g (0.24 mol) of **5** and 67 ml of 37% DCl aq solution was added sodium nitrite (20.4 g (0.30 mol)) and D_2O (37 ml) dropwise at 0 to 5 °C. The resulting diazonium salt solution was added dropwise to a solution comprising sodium sulfite (69.3 g), NaOH (13.7 g (0.34 mol)), and D_2O (340 ml) at 0 to 5 °C. Then, to the resulting solution was added 37% DCl (330 ml) under cooling by an ice bath, and additionally 37% DCl (67 ml) at 55 °C. The resulting mixture was stirred at between 70 and 80 °C for 10 min. After being cooled to room temperature, insoluble ingredients were filtered off, and the filtrate was neutralized by sodium carbonate. The resulting crystals were isolated by filtration and washed by ethyl acetate. Yield: 23.9 g (62.6%).

Synthesis of 3,5-Dimethyl-1-(4-nitrophenyl-2,3,5,6-d_4)pyrazole (D4): A mixture of 2,4-dioxopentane (8.2 g (0.082 mol)), **6** (11.7 g (0.075 mol)), and 12% DCl 120 ml were stirred at 80 °C for 5 h. Active carbon powder was then added to the resulting solution and stirred for 5 min. After filtration of the active carbon powder and other insoluble ingredients, to the filtrate was slowly added a solution comprising NaOH (19.3 g (0.48 mol)) and D_2O (73 ml) under cooling by an ice bath. The resulting crystals were isolated by filtration and washed by D_2O, and then recrystallized from 2-propanol three times. Yield 4.1 g (24.7%); mp = 102.0 °C; Deuterated ratio >99% (Deuterated ratio was determined by ^{1}H NMR comparing with methyl and pyrazole proton.); ^{1}H NMR ($CDCl_3$) δ=2.41 (3H, s), 2.55 (3H, s), 6.09 (1H, s), 7.70 (trace residual proton), 8.33 (trace residual proton).

3,5-Bis(methyl-d_3)-1-(4-nitrophenyl)pyrazole-4-*d* (D7) was synthesized in the same manner from **1** and 4-nitrophenylhydrazine. Mp = 101.5 °C; Deuterated ratio: methyl=91%, 4-position of pyrazole=98% (Deuterated ratio was determined by ^{1}H NMR comparing with phenyl proton.); ^{1}H NMR ($CDCl_3$) δ=2.28 (trace residual proton, m), 2.43 (trace residual proton, m), 6.11 (trace residual proton), 7.70 (2H, d), 8.33 (2H, d).

3,5-Bis(methyl-d_3)-1-(4-nitrophenyl-2,3,5,6-d_4)-pyrazole-4-*d* (D11) was synthesized in the same manner from **1** and **6**. Mp = 102.6 °C; Deuterated ratio: methyl=91%, 4-position of pyrazole=98%, phenyl >99%

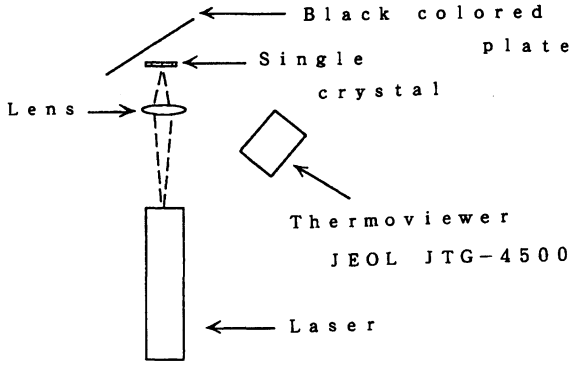


Fig. 10. A illustration of equipment for the temperature elevation measurements.

(Deuterated ratio was recognized as being the same as **D4** and **D7** at corresponding parts because of using the same starting materials); ^{1}H NMR (CDCl$_3$) $\delta=2.31$, 2.43, 6.10, 7.70, 8.33 (all of them are trace residual protons).

Crystal Growth. Single crystals of DMNP and their deuterated derivatives were prepared in a sealed glass tube by the Bridgmann–Stockberger method. A heater with three heating zones was used. The temperatures of the three zones were 120.5, 69.9, and 67.0 °C, respectively. The tube was moved down at a rate of 0.45 mm min^{-1}. Two weeks were necessary for completion.

Measurements. **IR Spectra:** IR spectra were measured with a Nicolet 5DX IR spectrometer. Samples were prepared as follows. To a mortar was measured 100 μl of a 2×10^{-2} mol dm^{-3} acetone solution of a compound and evaporated. Then, 3.31 mg of KBr was added and the ingredients were sufficiently mixed. All of the resulting mixture was used for a measurement.

Vis-NIR Spectra: Vis-NIR spectra were measured with a Hitachi U400 spectrophotometer. Samples of the crystals were prepared by cutting the above-mentioned large crystals to a thickness of about 3 mm along the plane of cleavage.

Temperature Elevation-Measurement: Experiments were carried out using the equipment shown in Fig. 10.

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