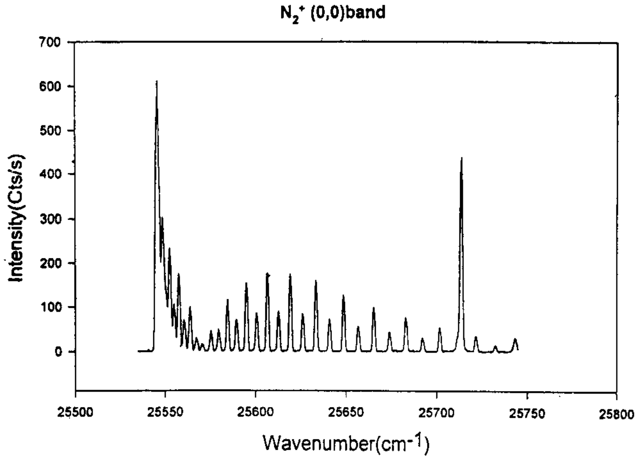

Figure 3. The vibronic emission spectra of gas phase N_2^+ generated in a jet by a corona discharge of the gas mixture of He and N_2. The spectrum shows the origin band in the transition of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$. The strong line at 25715 cm^{-1} is from the buffer gas He.

the the gas mixture of N_2 and the buffer gas He. The discharge conditions were adjusted for the maximum intensity of N_2^+ as well as the maximum value of N_2^+/N_2 in the spectrum observed. The maximum intensity of the N_2^+ was obtained at the 1.5 Torr of chamber pressure and 1050 V and 3 mA current. The rotational cooling was achieved employing a pinhole nozzle of 0.3 mm opening and 2.0 atm backing pressure. The supersonic beam could not be produced from the nozzle of smaller opening, since the sharpened anode partially blocks the pinhole during the operation. The visible emission spectrum shown in Figure 3 was taken by scanning 25,500 to 25,800 cm^{-1} at the step of 0.05 cm^{-1} and 50 μm of slit width over 10 min. This is assigned to the origin band in the transition[18] of $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$ of N_2^+ showing the intensity alternation due to the nuclear spin statistics of the homonuclear diatomic molecules as well as a bandhead in the P-branch which is very similar to that of the isoelectronic molecule CN.[19]

In summary, we have built in our laboratory the spectrometer for the vibronic emission spectra of transient molecules in the gas phase coupled with the technique of the corona discharge excited supersonic jet system. This exhibits the characteristics of simple, durable, and bright emission source for the high resolution vibronic spectra of unstable molecules.

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A Simple and Efficient Synthesis of Isatogens from 1-(o-Nitrophenyl)-1,3-butadiynes

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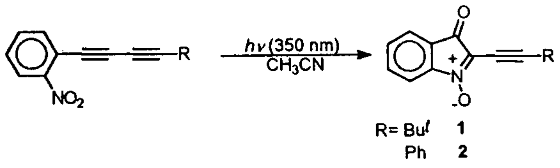
Irradiation of 1-(*o*-nitrophenyl)-5,5-dimethyl-1,3-hexadiyne (*o*-NDHD)[1~3] and 1-(*o*-nitrophenyl)-4-phenyl-1,3-butadiyne (*o*-NPPD)[4,5] in CH_3CN (2 mM) for 40 min yields isatogen derivatives **1** and **2** in high yields (Scheme 1).[6]



Scheme 1.

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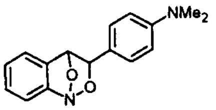
The photoreaction is very fast and efficient giving isatogen derivatives in 100% from *o*-NPPD and 51% from *o*-NDHD (49% *o*-NDHD was recovered) after only 40 min of irradiation in contrast to *o*-nitrostilbene[7~9] and *o*-nitrophenyl acetylene[9~12] which give low yields even after the long irradiation time. The photoreaction proceeds even under daylight since *o*-NDHD and *o*-NPPD absorb light of long wavelength. The color is changed into red when *o*-NDHD or *o*-NPPD solutions are kept under the daylight for several hours.

Splitter and Calvin[7] proposed an ionic mechanism for the photoreaction of *o*-nitrostilbene involving the intermediate **3** without any firm evidence. The photoreaction of *o*-nitrophenyl acetylene requires pyridine or similar basic solvents as catalyst,[10] because direct intramolecular cycloaddition of nitro group onto the carbon-carbon triple bond is forbidden by the Bredts rule.[11,13]



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The intramolecular photocycloaddition reaction of *o*-NDHD and *o*-NPPD proceeds in various solvents such as dry *n*-hexane, methylene chloride, ethanol, methanol, acetonitrile, and acetonitrile/water (1/1, v/v) and does not require any base such as pyridine.

The oxygen has no effect on the quantum yields of the formation of the compounds **1** and **2**, indicating that the photoreaction proceeds *via* the singlet excited state. Kinetic studies monitoring the remaining starting materials spectrophotometrically at various irradiation (at 365 nm) time show the reactions to be first order. The formation of isatogen derivatives was independent of the solvent polarity suggesting a radical mechanism and the formation of a neutral intermediate involving only one oxygen of the nitro group.

The photocyclization of *o*-nitrophenyl-1,3-butadiynes provides a simple, clean, and efficient synthetic method for isatogen derivatives in a very short reaction time. This method can be carried out in various solvents and the starting material can be quantitatively converted into isatogen derivatives. These isatogen derivatives can further be converted into isatogens with many interesting functional groups by manipulating the carbon-carbon triple bond in the molecules.

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Footnote

All new compounds were characterized by ^{1}H and ^{13}C NMR spectra.

Selected data for *o*-NDHD: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.02 (d, 1H), 7.54 (m, 3H), 1.26 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.1, 135.7, 132.8, 128.9, 124.7, 117.9, 95.7, 81.9, 70.4, 63.7, 30.2, 28.3 ppm; HRMS (M^+) calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0938.

o-NPPD: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.10 (m, 1H), 7.71 (m, 1H), 7.53 (m, 4H), 7.36 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 150.0, 135.8, 133.0, 132.6, 129.7, 129.3, 128.5, 124.9, 121.2, 117.7, 84.8, 81.5, 76.1, 72.9 ppm; HRMS (M^+) calcd for $C_{16}H_9NO_2$ 247.0633, found 247.0631.

1: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.58 (m, 4H), 1.60 (s, 9H) ppm; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 183.6, 147.1, 134.7, 131.5, 123.7, 122.3, 121.7, 120.5, 113.8, 65.9, 30.2, 29.0 ppm; IR ν_{max} (NaCl) 2970, 2207, 1714, 1403 cm^{-1}; HRMS (M^+) calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0954.

2: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.61 (m, 6H), 7.37 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 183.4, 147.3, 134.9, 132.1, 131.8, 130.0, 128.4, 123.6, 122.6, 122.0, 121.2, 114.1, 110.0, 75.7 ppm; HRMS (M^+) calcd for $C_{16}H_9NO_2$ 247.0633, found 247.0636.