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Color Reactions of Dinitrobenzyl Pyridine and Related Compounds

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Upon treatment with certain reagents, the photochromes, α- and γ-(2, 4-dinitrobenzyl)pyridine and 2, 4, 2′, 4′-tetranitrodiphenylmethane form stable, blue-colored compounds which probably have chromophoric structures similar to those of the photochromic modifications of the original compounds (two examples of the permanently colored compounds are the N-methyl bases and the products from reactions with epoxy compounds). Kinetic and spectrophotometric studies of these colored compounds and of the anions of the original photochromes are reported. These results are compared with data on the photochromic tautomers.

It is well known,[1] that α-(2, 4-dinitrobenzyl)-pyridine (α-DNBP) develops a deep blue color upon irradiation with ultraviolet light (4000 to 3000 Å) either in the crystalline state or in solutions. In the crystals, the blue color fades quite slowly in the dark but in solutions disappears rapidly (within a few milliseconds to a few seconds at room temperatures depending upon the solvent and the acidity). The γ isomer of DNBP shows the same behavior in solution, but the crystals are not phototropic.** The blue colored substances may also be generated chemically, but transiently, upon neutralization of the anions of the photochromic compounds.

In the present investigation, we continue our study of the photochromic reaction and its products, primarily through comparison with the ordinary chemistry of DNBP. This report covers the following:

A. Formation and properties of stable, conjugated molecular modifications of DNBP.
B. Spectral properties of these conjugated species.
C. Kinetic studies, including
   1. Formation of the DNBP anion in base solutions.
   2. Kinetics of the reaction of DNBP with epoxides.
   3. Comparison of the fading rates of the conjugated form of α- and γ-DNBP as produced chemically and phototropically.

Experimental

The γ-DNBP was prepared by the method[1b] already described. Carbon disulfide, benzene, and isooctane were of spectro grade, Matheson, Coleman and Bell, and carbon tetrachloride of spectro grade, Merck. All other chemicals were Eastman CP and were used without further purification.

To prepare the epoxy addition compounds, DNBP was dissolved in an excess of epichlorohydrin; this solution was used directly for some measurements. To prepare the solid for extinction measurements, the solution was allowed to reach equilibrium, i. e., the optical density reached a constant value, then the solvent was evaporated away under high vacuum. The resulting platelets were ground with KBr and pressed into pellets for the infrared spectra. Other samples of the platelets were dissolved in various solvents for taking spectral and reaction data.

The spectra were taken with a Cary 14 spectrophotometer, and the rate measurements were made by a "stop-flow method" with a detection system having a DuMont 6292 photomultiplier, a simple monochromater and a Speedomax recorder type C. The scanning beam was passed through a Corning glass filter 3-69 and a heat filter before entering a reaction tube. The schematic diagram of the reaction tube is shown in Fig. 1.

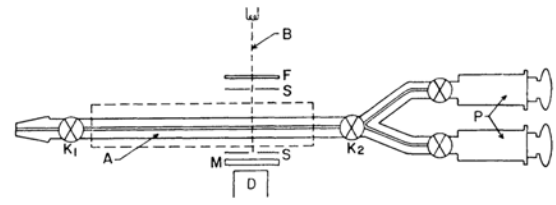

Fig. 1. Schematic diagram of stop-flow apparatus.

The reaction takes place in the 3 mm. capillary cell A, into which liquid is driven by the pressurized pistons P. Sequentially, the cell is evacuated through stopcock K_1, which is then closed; K_2 is opened and solutions flow from the separate cylinders, mixing at the tube junction. As the front of the rapidly moving

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1) a) A. E. Chichibabin, B. Kundshi and S. V. Benwalenskaja, *Ber. deut. Chem. Ges.*, **58**, 1580 (1925); b) R. Hardwick, H. S. Mosher ane P. Passailaigue, *Trans. Faraday Soc.*, **56**, 44 (1960); c) H. S. Mosher, C. Souers and R. Hardwick, *J. Chem. Phys.*, **32**, 1888 (1960); d) H. S. Mosher, R. Hardwick and D. Ben Hur, ibid., **37**, 904 (1962).

** We have found that liquid γ-DNBP is pale blue at its melting point[5] and that crystals immersed in H_2O or D_2O show blue color at even lower temperatures than the melting point. The α-isomer does not display these characteristics.

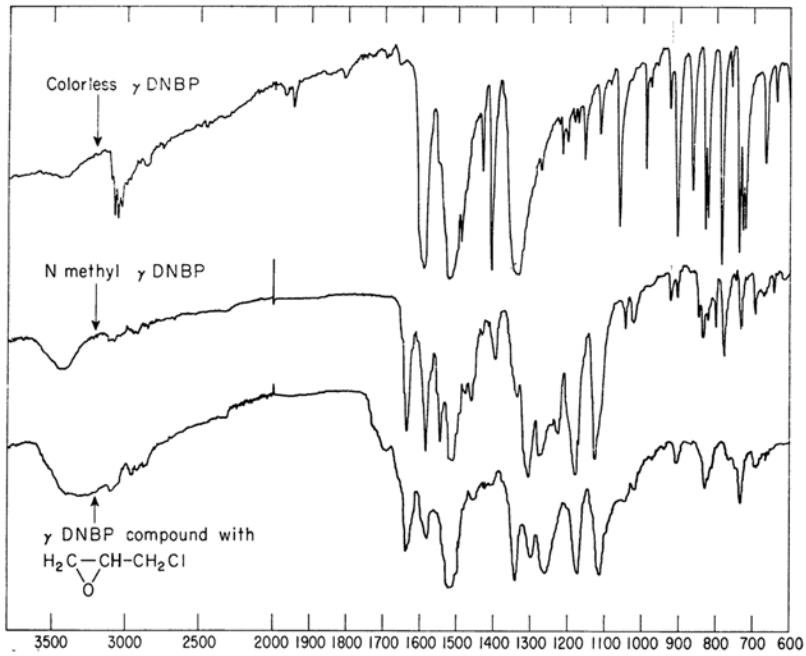


Fig. 2. Infrared spectra.

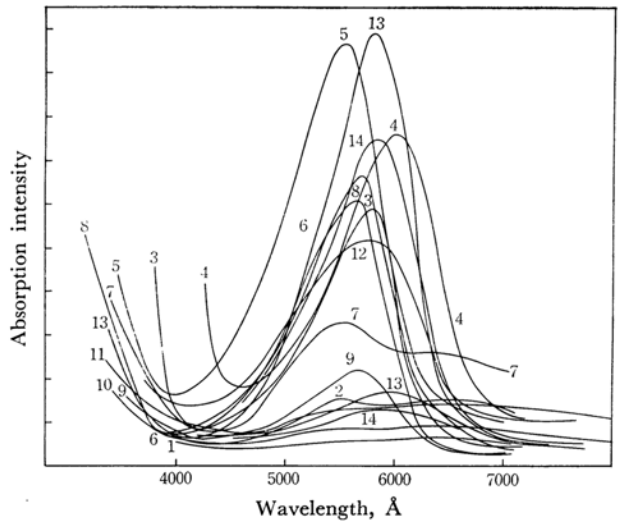


Fig. 3. Shift of visible spectra with solvent.

1	Isooctane	2	Cyclohexane	3	Carbon disulfide
4	Nitrobenzene	5	Carbon tetrachloride	6	C_6H_6
7	Freon 113	8	Mesitylene	9	*p*-Oxane
10	Isooctane	11	Heptane	12	Tetrahydrofuran
13	Acetone	14	Chloroform		

liquid passes the scanning beam, B, it triggers an oscilloscope monitoring device. M represents a monochromator while S indicates slits and F a filter.

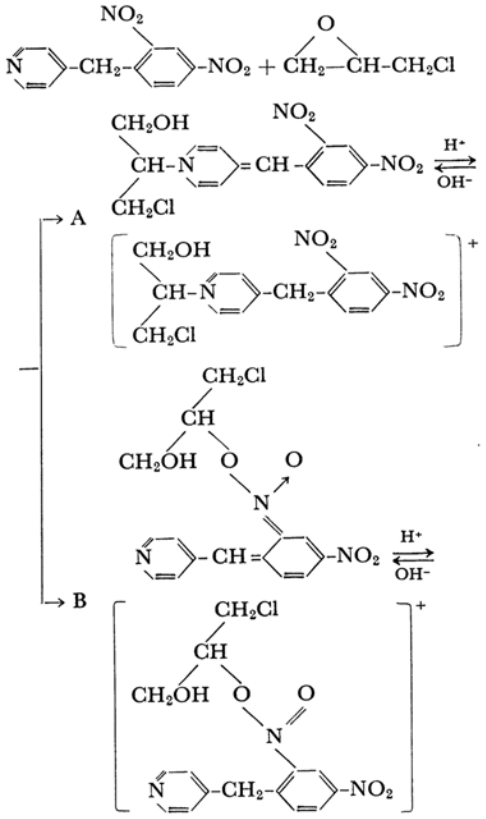
Results and Discussion

A. Stable Conjugated Compounds with Photochromic Absorption Spectra.—We have found that when dissolved in epoxy compounds such as epichlorohydrin, epoxy benzene, etc., such photochromic compounds as α-DNBP, γ-DNBP, and 2, 4, 2′ 4′-tetranitrodiphenylmethane acquire absorption spectra which are the same as those typical of their photochromic reactions. The blue colors formed by the photochromic substances and epoxy compounds are stable in the dark,

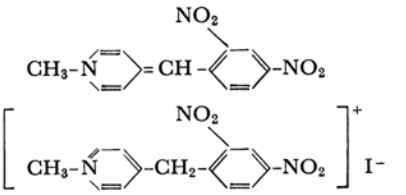
unlike those arising from photochromic reactions, although the former colors fade upon irradiation by near ultraviolet light. It is noticed that α-DNBP, and especially 2, 4, 2′, 4′-tetranitrodiphenylmethane, do not form the blue substance in as great an amount as that characteristic of γ-DNBP.

The nature of this visible absorption is probably the allowed transition, discussed below, which is also very likely the source of the photochromic colors. The blue color disappears upon the addition of H^+ and appears again upon the addition of OH^-.* The color appears more rapidly upon the addition of the epoxy compounds to the anions of the photochromic substances than to the neutral photochrome. In a solution originally neutral, the amount of H^+ necessary to destroy the blue color is just equivalent to the number of the moles of the photochromic substances contained.

One possibility for the reaction between γ-DNBP + epichlorohydrin is the following:



The fact that 2, 4, 2′, 4′-tetranitrodiphenylmethane also forms a blue substance in epoxy compounds, albeit with low intensity, indicates that B can not be neglected. However, the infrared spectrum of the blue substances, Fig. 2, clearly shows the $\equiv C-\overset{+}{N}\diagdown$ frequency at 1635 cm^{-1}, which is also found with similar intensity in



where ordinary DNBP does not have any absorption at this frequeccy. Although a C–O–N structure might possibly exhibit absorption at this energy, this more usually occurs at smaller frequencies, i. e., lower than 1600 cm^{-1}. We have prepared *N*-methyl γ-DNBP from γ-DNBP + CH_3I, followed by the addition of aqueous sodium hydroxide solutions; m. p. 161°C. The hydrogen bond frequency (3450 cm^{-1}) is displayed by crystals of the blue substance prepared from the solutions of γ-DNBP and epoxy compounds as well as in *N*-methyl γ-DNBP. The most characteristic feature in the infrared spectrum common to all the permanent blue modifications, (the epoxy complex and the *N*-alkylated compounds) is the near disappearance of the C–H stretching frequency peaks around 3000 cm^{-1}. The light induced and thermo-chromic blue mixtures show no detectable change at 3000 cm^{-1} presumably because only a very small proportion of the compound is changed.

B. Visible Absorption Spectra of the Conjugated Compounds.—In the process of taking extinction coefficients of the product of γ-DNBP and epichlorohydrin, we made Beer Law plots by successively diluting solutions which were prepared by dissolving crystals of the product in isopropyl alcohol. These gave curves which were linear within our experimental error of about 1%. From these measurements, the calculated decadic extinction coefficient was 2.40×10^4 l./mol.-cm. at the absorption peak at 5880 Å, taken on the basis of 100% conversion.*

As we have seen, the two rings of γ-DNBP may also be coupled through methylation of the ring nitrogen, giving a deep blue solution. As with the epoxide complex, this blue product shows a peak at 5800 Å; its decadic extinction coefficient is 2.4×10^4 l./mol.-cm. for the γ-isomer and 1.97×10^4 l./mol.-cm. for the α-isomer.

So far, we do not know the extinction coefficient

* The appearance of blue color is immediate when base is added to an acidified solution of DNBP-epoxy compound, even though the original reaction between DNBP and epoxy is usually very slow. For this reason, we feel that the DNBP-epoxy compound is not decomposed by acid and reconstituted by base, but that it merely assumes a colorless, cationic form in the presence of acid.

* We believe that the equilibrium between γ-DNBP and epichlorohydrin favors almost complete formation of the complex. The reasons for this conclusion are that the extinction coefficient of the complex (calculated on 100% conversion) is the same as that of the *N*-methyl base (see below), which has a similar absorbing structure. Moreover, when the complex is isolated by pumping off the solvent, no trace of the original γ-DNBP remains.

The fact that Beer's Law is followed to extreme dilution by both alcohol and epichlorohydrin solutions of the blue compound argues that the equilibrium constant of the reaction of γ-DNBP + epichlorohydrin must be extremely high.

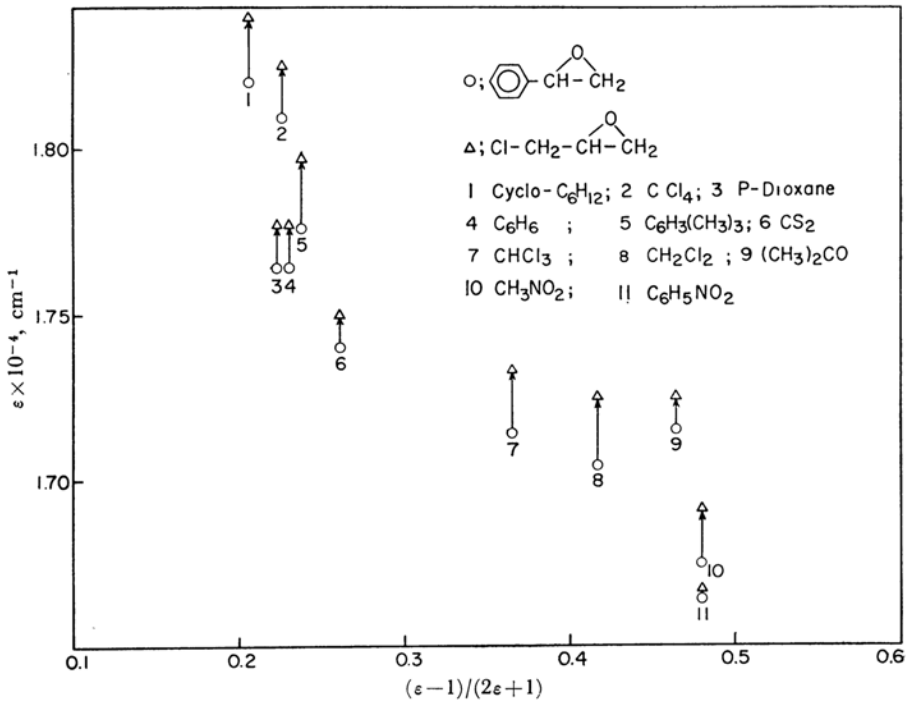


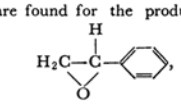
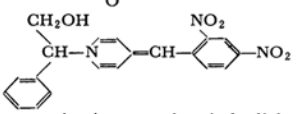
Fig. 4. Relation between frequency shift and dielectric constant.

of the blue photochromic product of γ-DNBP, but it is reasonable to believe that it might very well be approximately the same as that of the conjugated structure produced by either of the permanent chemical reactions discussed above. If we take this assumption, however, we find that the amount of photochromic conversion in solutions of γ-DNBP (or for that matter in either the crystalline form or the solutions of α-DNBP) can be only a few percent. As proposed in an earlier paper of this series, this effect may arise from a photoequilibrium which is established through the destruction of the blue tautomer by radiation in the ultraviolet region (all the photochromic products are stable to irradiation at 5800 Å). We are continuing to investigate this possibility.

The maximum color density developed by either α-DNBP or 2, 4, 2′, 4′-tetranitrodiphenylmethane in epichlorohydrin never even remotely reaches that shown by the gamma isomer, the "apparent" decadic extinction coefficients being only 53 l. mol^{-1} cm^{-1} and 9.3 l. mol^{-1} cm^{-1} respectively at 36°C. Since we know of no obvious reason why the conjugated forms of these two substances should not have approximately the same absorption efficiency, we believe that the effect must be caused in the former compounds by incomplete dissociation of the bridge hydrogen or by the existence of an equilibrium which is not favorable to the product formed with epichlorohydrin.

We have found that the color formed by γ-DNBP and various epoxy compounds shifts from blue to pink as the original product is diluted with solvents of decreasing dielectric constant. Figure 3 shows several spectra of solutions made up by mixing 10 ml. of various solvents with 0.1 ml. of a solution consisting of 10^{-3} mol. of γ-DNBP in 1 ml. of epichlorohydrin;* it may be seen that the absorption curve moves to longer wavelengths with increasing dielectric constant of the medium. This red shift would be expected if the excited state of the absorbing molecule were to be of a more polar nature than the ground state, i. e., increasing interaction with the solvent would lower the energy of the excited state. One transition which would fulfill this requirement is that to the antibonding π^* state.

According to theory,[2] the relative frequency shift of the absorption, $\Delta\nu/\nu$, of a vibrating dipole in a spherical cavity of radius a, surrounded by a continuum of dielectric constant ε, is proportional to $(\varepsilon-1)/(2\varepsilon+1)\cdot(1/a^3)$. In Fig. 4, the

* Similar results are found for the product of the reaction between γ-DNBP and  , i. e., possibly 

Since the added benzene ring is not conjugatively linked to the DNBP structure, it does not directly influence the $\pi^*\leftarrow\pi$ transition.

2) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York (1962), pp. 190, 222.

maximum absorption frequency of the γ-DNBP epoxy compound is shown as a function of $(\varepsilon-1)/(2\varepsilon+1)$ of the solvent. The approximate linear relationship suggests that the absorption may be the $\pi^*\leftarrow\pi$ transition of the conjugated system.

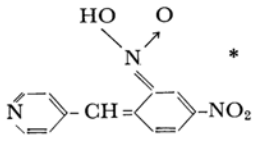
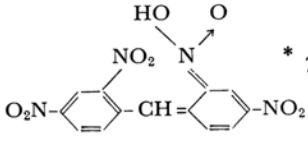
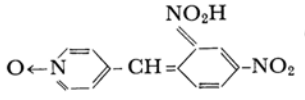
If the solutions are made using solvents with very weak intermolecular forces: e. g., isooctane ($\delta=6.9$), freon 113 ($\delta=7.3$) and cyclohexane ($\delta=8.2$), there appear two maximum absorption peaks, which are not found in the solvents with solubility parameter[3] higher than carbon tetrachloride ($\delta=8.6$). In these bifurcated spectra, the absorption peak of shorter wavelength, ~5400 Å or less may correspond to the absorption found in the other solvents; however, the long wavelength peak, 6000 to 7000 Å, is probably different in nature, because even in the highly polar solvents no absorption has been found in this region. The latter transition may arise from dimers or higher aggregates which could not be dispersed to monomer form owing to the weaker intermolecular forces of the solvents.

The absorption wavelength arising from the transiton of a π-electron to its first excited state is given by the free electron model[2] as:

$$\lambda=\frac{8ma^2C}{(2k+1)\boldsymbol{h}}$$

where a is the length of the potential well, k the number of orbitals occupied by the π-electrons in the conjugated systems, m the electron mass, C the light velocity, and $\boldsymbol{h}$ Planck's constant. In applying the free electron theory to our systems there are very serious problems of hetero atoms with different electronegativity; however as a zeroth order approximation, we neglect this difference. Taking an average C–C bond distance of 1.4 Å and those of C–N and of N–O as 1.2 Å we obtain the following results for the neutral conjugated systems and for the anion (in the latter, we use k_N+1 to account for the extra electron), Table I.

TABLE I. CALCULATED AND EXPERIMENTAL ABSORPTION WAVELENGTHS

Species	Absorption wavelength mμ: Neutral molecule Calcd.	Neutral molecule Obs.	Anion Calcd.	Anion Obs.
 *	585	575	585 500	640 480
 *	700	712	700 610	700 —
	690	650 527	690 590	650 527

* Shown as one of the possible photochromic modifications.

In the anion, calculations are made for transition of the extra electron ($n=6$ to $n=7$) and again for the optical electron as in the neutral molecule ($n=5$ to $n=6$); this action is supported by the double peak found in the anion spectrum. It may be seen that, at least in the neutral molecule, the free electron theory makes a fairly good prediction of the wavelength which is observed, thus lending support to the proposed structures and to the assignment of $\pi^*\leftarrow\pi$ for the transition. In the 585 mμ band for γ-DNBP it is noticed that, although the agreement between calculation and experiment is good for the neutral molecule, in the anion the discrepancy runs to ~65 mμ. This misbehavior of the ion may be due to large solvation effects arising out of the fact that the anion has a charge. The agreement of the calculated wavelengths and the observed ones is excellent when we consider the approximation used. Probably this is largely fortuitous, yet the evidence does support the conclusion that the absorption is due to the $\pi^*\leftarrow\pi$ transition.

When the anions of γ-DNBP are diluted with certain polar solvents such as nitromethane or *p*-dioxane, the characteristic green color disappears, and the typical blue-violet color of the neutral conjugated systems appears transiently. This may possibly be caused by transfer of the excess charge from the anion to the solvent. In acetone, however, a stable pink color gradually appears, Figure 5, possibly arising from complex formation.

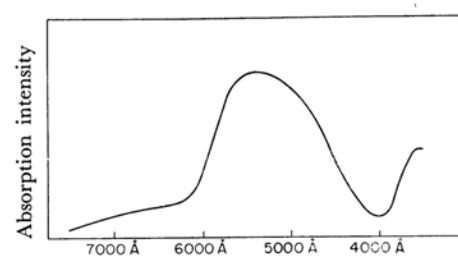


Fig. 5. Spectrum of pink solution of DNBP anion in acetone. (Concn. 2.08×10^{-7} mol./l.)

C. Kinetic Studies. — *1) Anion Formation Reaction.*—The rates of formation of the anions of DNBP have been measured with the "stop-flow method." Typically, α-DNBP solution of 1.07×10^{-4} mol. dissolved in 25 ml. of isopropanol was mixed in the reaction tube with an aqueous solution of 0.098 molar sodium carbonate. The relative proportions of DNBP solution to base solution varied from 1.0 to 2.0; however, the rate

3) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall Inc., New Jersey (1962).

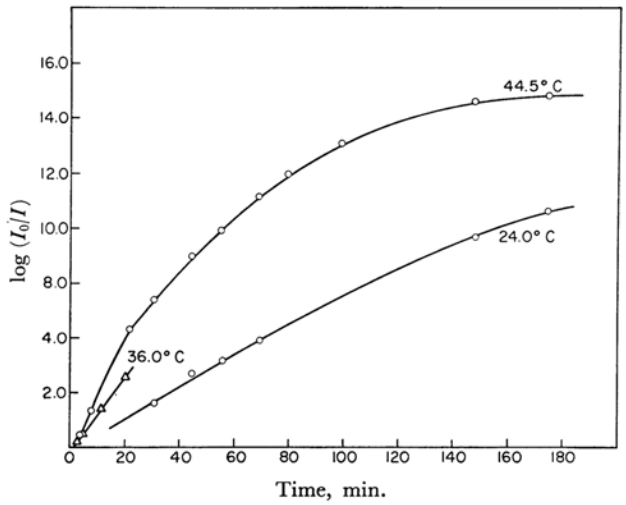


Fig. 6. Reaction rate of γ-DNBP+Cl·CH_2·CH·CH_2·O.

constants measured did not change in this range of concentration. The final pH of the one-to-one solution was 12.8. The rate of formation of the anion was found to follow first order kinetics under our conditions of a large excess of base. Sample rates of anion formation in solutions of α-DNBP mixed with sodium hydroxide are shown in Table II. With OH^- in excess, our observed rate constant is given by:

for α-DNBP

$$k_{\text{anion}}=1.29\times10^{6}\exp\left(-\frac{10.5\times10^{3}}{RT}\right)\text{sec}^{-1}$$

Table II. The rate of formation of anions from α-DNBP+aq. NaOH

Concn. of α-DNBP in isopropanol; 3.8×10^{-6} mol./ml., pH of aq. NaOH=12.0

Temp. °C	Vol. of α-DNBP / Vol. of aq. NaOH	$\tau_{1/2}$ sec.	k sec^{-1}
27.5	0.50/0.50	24.8	2.80×10^{-2}
27.0	0.45/0.50	23.6	2.94×10^{-2}
27.0	0.40/0.60	23.6	2.94×10^{-2}
27.0	—	23.6	2.94×10^{-2}
26.5	0.45/0.55	24.0	2.89×10^{-2}
36.0	0.40/0.65	16.5	4.20×10^{-2}
37.0	0.35/0.60	13.8	5.03×10^{-2}
37.0	0.65/0.55	14.1	4.92×10^{-2}
43.0	0.45/0.55	9.2	7.55×10^{-2}
43.0	0.45/0.50	8.2	8.46×10^{-2}
43.0	0.50/0.60	11.0	6.30×10^{-2}
43.0	0.45/0.60	10.0	6.94×10^{-2}
15.5	0.35/0.50	38.0	1.825×10^{-2}
14.5	0.30/0.50	42.2	1.644×10^{-2}
16.0	0.40/0.60	37.4	1.735×10^{-2}
16.0	0.40/0.50	32.0	2.165×10^{-2}

and for γ-DNBP

$$k_{\text{anion}}=2.82\times10^{7}\exp\left(-\frac{11.2\times10^{3}}{RT}\right)\text{sec}^{-1}$$

2) Reaction of DNBP+Epoxy Compounds.— α-DNBP and γ-DNBP were dissolved in pure Cl·CH_2·CH·CH_2O and the rates of formation of the blue conjugated compounds were measured by following the absorption intensity at the wavelength of the maximum absorption. It was found that the rate followed 1st order kinetics. The results are given by the following:

for α-DNBP

$$k=5.4\times10^{4}\exp\left(-\frac{13.6\times10^{3}}{RT}\right)\text{sec}^{-1}$$

for γ-DNBP

$$k=1.06\times10^{3}\exp\left(-\frac{12.6\times10^{3}}{RT}\right)\text{sec}^{-1}$$

It is seen that the reaction, α-DNBP+$ClCH_2$·$CHCH_2O$ requires a slightly higher activation energy than that of γ-DNBP+$ClCH_2$·$CHCH_2O$, but the former has the higher frequency factor, probably due to the proximity of nitrogen atom in pyridine ring to $-CH_2-$ bridge. As mentioned earlier, the equilibrium is far more favorable to the formation of the conjugated system in γ-DNBP than in α-DNBP.

3) Study of the Conjugated Form of γ-DNBP as Produced Chemically and Phototropically.— Other work in this laboratory[4] has shown that when the brown-green anion of γ-DNBP is neutralized, the blue color, characteristic of the phototropic modification, appears fleetingly before the solution becomes colorless. We feel that it

is reasonable to assume that the species which gives the blue color upon neutralization may very well be the same as that which arises photochemically, thus we are attempting to compare the two in as many ways as possible. The previous report has discussed the low temperature decay rates and spectra of the two systems of γ-DNBP, the discussion below gives rates at higher temperatures and compares activation energies for the fading of the systems as produced chemically and phototropically.

This experiment was made by mixing solutions of γ-DNBP anion with HCl solutions, the concentrations being adjusted such that the pH of the final mixtures came very near to pH=7. In order to increase the solubility of γ-DNBP, isopropanol was added, the concentration of which was 25% of the final solution upon neutralization, With these conditions we have found the following results, Table III.

Table III. Fading-rate of the blue, conjugated form as chemically produced

Temp., °C	k, sec^{-1}
11.0	0.56 ± 0.09
2.1	0.14 ± 0.02

It has been reported previously[4] that the rate of the disappearance of the blue, colored form of γ-DNBP chemically produced was about 2×10^{-3} sec^{-1} at 173°K. By combination with this result, we may calculate the activation energy to be 5.0×10^3 cal./mol. for the fading rate. This value may be compared to that of 4.5×10^3 cal. reported earlier[5] for the fading of the phototropic blue γ-DNBP in tetrahydrofuran solutions. The comparison is only approximate because of the differences in solvent and the sensitivity of the stop-flow measurements to small errors in pH adjustment, but taken with other reported similarities, this agreement again supports the argument that the chemically and phototropically produced species are identical.

This research was supported by the Atomic Energy Commission under Contract No. AT(11-1)-34, Project 88. We also gratefully acknowledge many conversation, suggestions and other valuable contributions made by Professor Harry S. Mosher.

4) R. Hardwick and H. S. Mosher, *J. Chem. Phsy.*, **36**, 1402 (1962).
5) H. Hiraoka and R. Hardwick, ibid., **41**, 2568 (1964).