

A LUMINESCENCE AND FLASH PHOTOLYSIS STUDY OF THE PHOTOSENSITIZER N-METHYL-2-BENZOYL- β -NAPHTHIAZOLINE

GÖRAN RÄMME

Institute of Physical Chemistry, University of Uppsala, P.O. Box 532, S-751 21 Uppsala (Sweden)

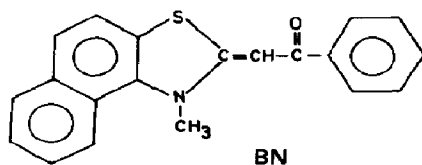
(Received November 25, 1977; in revised form February 7, 1978)

Summary

Results of luminescence measurements on N-methyl-2-benzoyl- β -naphthiazoline (BN) in solution at room temperature and in a rigid glass matrix at 77 K are presented. The lowest triplet state of BN corresponded to an energy of 54.3 kcal mol⁻¹ with a lifetime of 0.20 s at 77 K. By means of a series of flash photolysis experiments in tetrahydrofuran and ethanol, absorption from a transient species was observed in the 430 - 1000 nm wavelength region and this has been attributed to triplet-triplet absorption from the molecule. Rate constants for the disappearance of the triplet of BN in these solvents have also been elucidated. Efficient quenching of the triplet state of the compound by molecular oxygen is reported and a quenching constant $k_q = 6.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was determined in ethanol.

1. Introduction

Photosensitized oxidation of polymers is important industrially [1, 2]. Recently it has been reported that N-methyl-2-benzoyl- β -naphthiazoline (BN)



is a very effective sensitizer for the photocrosslinking of poly(vinyl cinnamate) [3] and for the photo-oxidative degradation of polyethylene [4] and polydienes [5]. It was consequently important to examine this sensitizer from a photochemical point of view. The results of a series of luminescence and flash photolysis experiments are reported below. A long lived emission was observed at low temperature and identified as the phosphorescence spectrum, and a short lived transient species was generated by flash photolysis at room temperature. This species has tentatively been assigned to the BN molecule

in its lowest excited triplet state. In addition quenching of the triplet by oxygen is reported.

2. Experimental

The flash photolysis experiments were carried out with flash apparatus number V described elsewhere [6]. It can store a maximum energy of 8 kJ at 6.4 μF and 50 kV and the flash time measured at halfwidth is about 10 μs . A flash energy of 1.4 kJ was used throughout the experiments unless otherwise stated. The photolysis was conducted in a 10 cm glass cell having a diameter of 2.0 cm. The cell was part of an all-glass apparatus which could be connected to a high vacuum line. The stock solution was degassed by means of a number of efficient freeze-thaw cycles. The cell device was detached from the vacuum line and the solution to be flashed was prepared by first distilling the solvent and then pouring the required amount of the remaining solution into the cell to achieve the desired concentration of about 2×10^{-6} M. When necessary this procedure was repeated to obtain a fresh solution prior to a new photolysis experiment.

In the oxygen quenching experiments, an ampoule containing oxygen of known pressure and temperature was prepared and attached to the flash cell apparatus. The method described above was used to prepare the dilute solution to be flashed. Since the ratio between the volume of the ampoule and the entire volume of the cell device above the solution was known, the initial pressure of oxygen could be calculated.

The solution to be photolysed was shielded from light from the analysing beam of the XBO 450 W xenon lamp by means of a Jena^{ex} GG 14 filter which excluded light of wavelengths shorter than 500 nm. The photoelectric signal was fed into a Tektronix 533 oscilloscope. Spectral and kinetic information was provided from enlarged photographs of the transient signals displayed on the oscilloscope screen.

In the kinetic studies the time-resolved phosphorescence measurements were carried out with a commercial photoflash lamp with a flash time duration of about 100 μs . An excitation filter, Jena^{ex} UG 2, transmitting light between 300 and 400 nm was inserted between the lamp and the sample compartment. The degassed solution of BN in a 5:5:2 mixture of ether, isopentane and ethyl alcohol (EPA) was contained in a sealed glass tubing which fitted into a finger at the bottom of an all-glass Dewar vessel. The low temperature cell device was placed in a holder, liquid nitrogen was introduced and the rigid glass solution was exposed to the flash light. The emitted light was focused on the entrance slit of a Zeiss M 4 Q II monochromator and entered a Hamamatsu R 213 photomultiplier tube after traversing the dispersing medium. The photoelectric signal produced was displayed on a Tektronix 533 oscilloscope and the transient curves were treated as before.

The spectral luminescence measurements were conducted using an excitation system composed of a water-cooled high pressure SP 500 W

mercury lamp followed by a water-cooled Jena[®] UG 2 filter. The detecting system was the same as that mentioned above except that the oscilloscope was replaced by a Zeiss P M Q II indicator instrument.

The spectrophotometric measurements were performed using a Zeiss DMR 10 spectrophotometer.

3. Materials

The BN was kindly supplied by Dr. Jan F. Rabek (originally a gift from J. Williams, Kodak, Rochester, N.Y. [3]) in the form of yellow crystals (melting point, 116 °C) and used without further purification.

Tetrahydrofuran (THF) (Merck, pro analysis) and spectroscopic ethanol (99.5 vol. %, Kemetylabs.) were distilled, the middle fraction being used.

4. Results and discussion

4.1. Luminescence measurements

Figure 1 shows the absorption spectrum of BN in spectroscopic ethanol. It consists of three intense and one weak absorption bands in the UV and visible spectral regions. Table 1 gives the wavelengths of maximum intensity and the corresponding extinction coefficients in ethanol and THF. The magnitude of the extinction coefficients and the wavelength shifts upon changing solvent polarity indicate that the 325 nm band may represent an $n \rightarrow \pi^*$ transition and the 400 nm band a $\pi \rightarrow \pi^*$ transition.

The fluorescence spectrum from an air-saturated 2×10^{-4} M solution of BN in ethanol at room temperature and the long wavelength absorption band of the molecule are shown in Fig. 2. The emission spectrum has a maximum intensity at a wavenumber of $\bar{\nu} = 21.0 \times 10^3 \text{ cm}^{-1}$. The ordinate of the

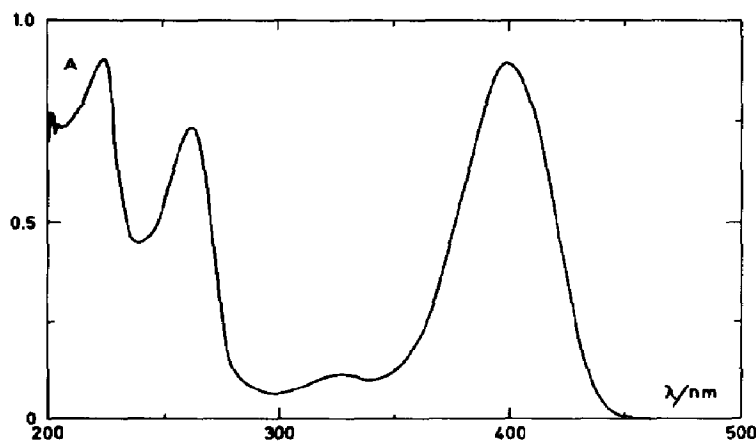


Fig. 1. Absorption spectrum of a 2.1×10^{-5} M solution of BN in spectroscopic ethanol.

TABLE 1
Extinction coefficients for BN in ethanol and THF

Ethanol		THF	
λ_{\max} (nm)	$\epsilon \times 10^{-4}$ ($M^{-1} \text{ cm}^{-1}$)	λ_{\max} (nm)	$\epsilon \times 10^{-4}$ ($M^{-1} \text{ cm}^{-1}$)
224	4.0		
262	3.3		
325	0.43	332	0.57
400	4.1	396	3.9

spectrum is presented as relative fluorescence intensity I_{rel} obtained from the instrument reading I' by correction for the photomultiplier sensitivity $P(\tilde{\nu})$ and the spectral bandwidth $\Delta\tilde{\nu}$ according to

$$I_{\text{rel}} = \frac{I'}{P(\tilde{\nu}) \Delta\tilde{\nu}} \quad (\text{I})$$

When the same experiments were performed using an oxygen-free solution of the same concentration, the intensity of the fluorescence spectrum increased by about 15% which demonstrates that oxygen quenches the singlet state to some extent.

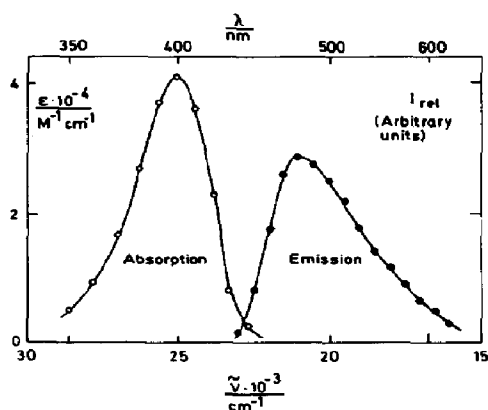


Fig. 2. Fluorescence spectrum and part of the absorption spectrum of an air-saturated 2.4×10^{-4} M solution of BN in spectroscopic ethanol measured at room temperature.

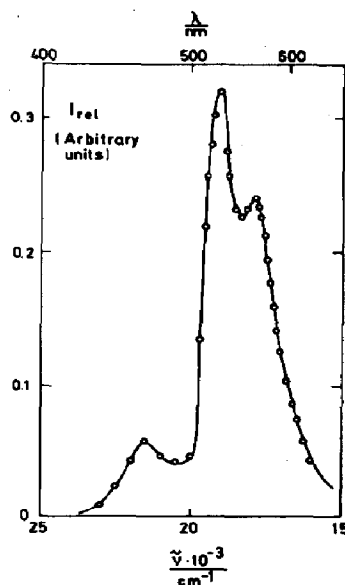


Fig. 3. Observed total emission spectrum of a 2.4×10^{-4} M solution of BN in degassed rigid glass EPA solution at 77 K.

The luminescence spectrum from a 2×10^{-4} M solution of BN in a degassed EPA rigid glass solution at 77 K is similarly presented in Fig. 3. It shows two main bands, a weak one having a maximum intensity at $\bar{\nu} = 21.5 \times 10^3 \text{ cm}^{-1}$ and an intense one composed of sharp peaks at $\bar{\nu} = 19.0 \times 10^3$ and $17.8 \times 10^3 \text{ cm}^{-1}$, respectively. No change in the intensity of the spectrum was noticed when the solution was examined under the same conditions after air saturation. Measurements at room temperature in an oxygen-free solution with otherwise unchanged experimental conditions gave only the first emission band, with an intensity of only about 1% of that obtained at low temperature. In addition, flash excitation of the solution at low temperature revealed only the structured emission band. This appeared in the second time region and no emission could be detected at wavenumbers $\bar{\nu} > 20.0 \times 10^3 \text{ cm}^{-1}$. From these results it is concluded that the emission band centred at $\bar{\nu} = 21.5 \times 10^3 \text{ cm}^{-1}$ can be attributed to the fluorescence and that the structured band represents phosphorescence from the lowest triplet state.

Applying an ordinary first order kinetic treatment to the decay of the phosphorescence gave a linear relation with a rate constant $k_1 = 5.0 \text{ s}^{-1}$ corresponding to a lifetime of the lowest triplet state of $\tau = 0.20 \text{ s}$ in the rigid glass matrix.

4.2. Flash photolysis of BN in the absence of oxygen at room temperature

In the first series of flash experiments the compound was dissolved in THF, the solution carefully degassed and flash excited in the 396 nm band. A slight permanent photochemical removal of BN was observed in the absence of oxygen. Each flash caused about 1% decrease of the 396 nm absorption band. The photolysis created a transient species which absorbed in the wavelength region 430 - 1000 nm. Figure 4 shows the signal at 620 nm from a 2.5×10^{-6} M THF solution using a flash energy of 1.4 kJ. The following observations support the assignment of the transient absorption to the triplet-triplet transition of BN. The signal was quenched by oxygen. No transient species were observed upon flashing the compound dissolved in the heavy-

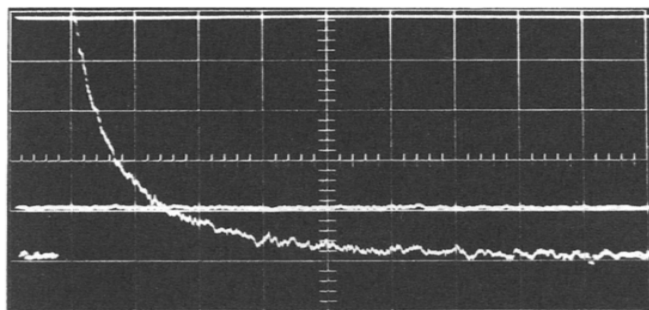


Fig. 4. Typical oscilloscope tracing at 620 nm of the transient appearing in flashing a 2.5×10^{-6} M solution of BN in THF using a flash energy of 1.4 kJ. The time scale is $200 \mu\text{s}$ per division and the time constant of the electrical circuit is $10 \mu\text{s}$.

atom solvent chloroform. In addition the absorption signal was found to reach its peak intensity value shortly after that of the flash and to return to the level prior to the flash. The triplet spectrum was measured at 50 μ s and is presented in Fig. 5. It consists of two distinct bands, a narrow one with maximum intensity at 440 nm and a broad one with maximum at 640 nm. The extinction coefficient of the triplet-triplet absorption was calculated by comparing, at corresponding times after the flash, the amount of transient absorption increase at 640 nm and the depletion of the ground state absorption band at 420 nm. A correction for the triplet-triplet absorption at 420 nm was introduced by utilizing the absorption value at 460 nm and assuming a symmetrical band around the peak intensity at 440 nm where no interference with the singlet absorption spectrum occurs. Thus a calculation of the triplet extinction coefficient at 640 nm at different points of time after the flash using $\epsilon_S^{420} = 1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was found to give a constant value of $\epsilon_T^{640} = 1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.

In order to determine the rate constants for the disappearance of the triplet species the kinetics were monitored at 620 nm. Under the present experimental conditions the disappearance can be fully explained by the two parallel reactions



where T denotes the lowest triplet state and S_0 the ground state. The concentration of BN was sufficiently low for neglect of the reaction between triplet and ground state molecules. Thus the rate constants k_1 and k_2 can be evaluated from the differential equation

$$-\frac{d[T]}{dt} = k_1 [T] + k_2 [T]^2 \quad (II)$$

The rate constant k_1 was determined from a transient curve recorded at a flash energy of 400 J, at which the concentration of the triplet species produced is sufficiently low to prevent triplet-triplet quenching.

The second term in eqn. (II) can thus be neglected and a value $k_1 = 2.6 \times 10^3 \text{ s}^{-1}$ was calculated from a plot of $\ln [T]$ versus time. At higher flash energies, *i.e.* 1.4 kJ, the concentration of the triplet state is considerable and the complete solution of eqn. (II) must be considered, namely

$$\frac{[T]_0 - [T]}{[T]_0} = \frac{1 - \exp(-k_1 t)}{1 - \{k_2 [T]_0 \exp(-k_1 t)\} / (k_1 + k_2 [T]_0)} \quad (III)$$

Here $[T]_0$, the zero-time triplet concentration, has been arbitrarily chosen as the concentration at 50 μ s after flash initiation, *i.e.* when the flash is over. Hence a plot of $[T]_0 \{1 - \exp(-k_1 t)\} / ([T]_0 - [T])$ versus $\exp(-k_1 t)$ should give a straight line of slope $-k_2 [T]_0 / (k_1 + k_2 [T]_0)$. Figure 6 reveals that this treatment gives a linear relation and a value of the rate constant $k_2 = 0.8 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ was calculated using $\epsilon_T^{620} = 1.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The

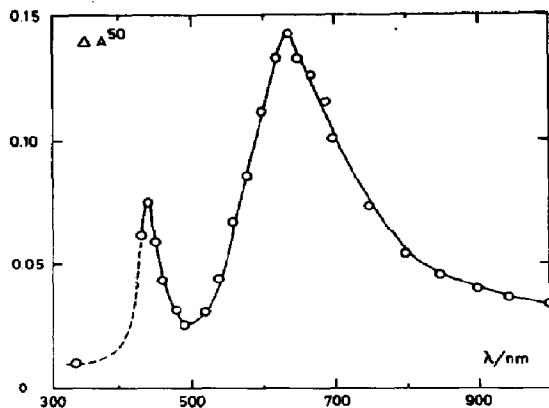


Fig. 5. Difference spectrum (solid curve) presented as the change in optical density *vs.* wavelength, showing the triplet absorption from the photolysis of a 2.4×10^{-6} M solution of BN in THF at room temperature. The spectrum was measured after 50 μ s and the flash energy was 700 J. The broken curve shows the singlet depletion region (extrapolated).

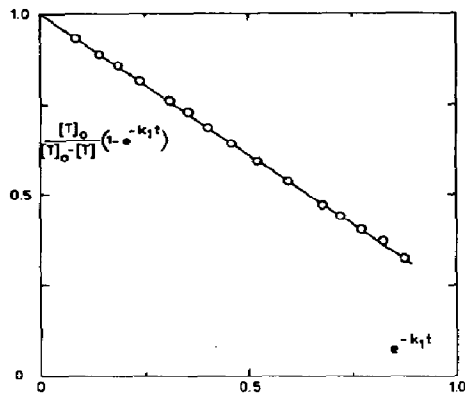


Fig. 6. A combined first and second order treatment of the kinetics of the triplet decay at 620 nm upon flash excitation of BN in THF. See the text for explanation of the coordinate axes.

result is of the same order of magnitude as the theoretically determined rate constant for a second order diffusion-controlled reaction calculated from $k_a = 8RT/3000\eta$, giving $1.3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

The same kinetic behaviour was obtained when the 440 nm band was analysed. This indicates that the entire transient spectrum recorded originates from the same species, *i.e.* the triplet state of BN.

The transient spectrum was also observed in degassed ethanol solution. The shape was similar to that found in THF except that the narrow peak at 440 nm was not observed. A possible reason is that the red shift of the singlet spectrum and a blue shift of about 10 nm of the triplet spectrum may have caused a displacement of the peak in question into the singlet absorption region where its detection is precluded.

A different kinetic behaviour was observed in ethanol. The transient signal was found to decay much more rapidly in this solvent than in THF. The lifetime, measured at half peak intensity, was 50 μ s in ethanol compared with 150 μ s in THF. First order kinetics were obtained and a rate constant of $2.1 \times 10^4 \text{ s}^{-1}$ was determined. No change in the absorption spectrum of BN was noticed after repeated flashing, indicating low photochemical reactivity under these conditions.

Flash excitation of BN was also performed in methanol. Although the triplet state was produced in this solvent, the rate of disappearance was found to be close to the lifetime of the flash. A reliable value of the rate constant could therefore not be determined.

The spectral information reported has been collected in Fig. 7 which depicts the energy levels for the observed transitions in BN. The lowest triplet

level T_1 has an energy of $\nu = 19\,500\text{ cm}^{-1}$ ($54.3\text{ kcal mol}^{-1}$) and a singlet-triplet splitting ΔE (S_1-T_1) of 6000 cm^{-1} was found. In addition the observed vibrational splitting of the S_0 level was 1200 cm^{-1} .

4.3. Quenching by oxygen

By means of spectrophotometric measurements, it was confirmed that repeated flash treatment of an air-saturated solution of $2.5 \times 10^{-6}\text{ M}$ BN in ethanol caused no permanent changes in the absorption spectrum of the compound. Thus low photochemical reactivity was observed under these conditions. Furthermore, in the presence of added amounts of oxygen, the decay rate of the triplet was unchanged when the solution was subjected to consecutive flashes, indicating that oxygen is not appreciably consumed by BN or the solvent during observations. The decay of the triplet BN can thus be described by the following expression:

$$k_{\text{obs}} = -\frac{d\ln[T]}{dt} = k_1' + k_q[\text{O}_2] \quad (\text{IV})$$

A plot of the observed first order rate constant k_{obs} versus concentration of oxygen is depicted in Fig. 8. A good linear relation is obtained, which demonstrates that eqn. (IV) is justified, and a value of the quenching constant $k_q = 6.6 \times 10^{10}\text{ M}^{-1}\text{ s}^{-1}$ was determined. The concentration of oxygen in the solution was calculated using the solubility coefficient $\lambda_{\text{et}}^{22} = 0.275$ [7]. The quenching constant is about one order of magnitude higher than that predicted for a corresponding bimolecular diffusion-controlled reaction. It is thus possible that the quenching mechanism is of the long-range Förster type

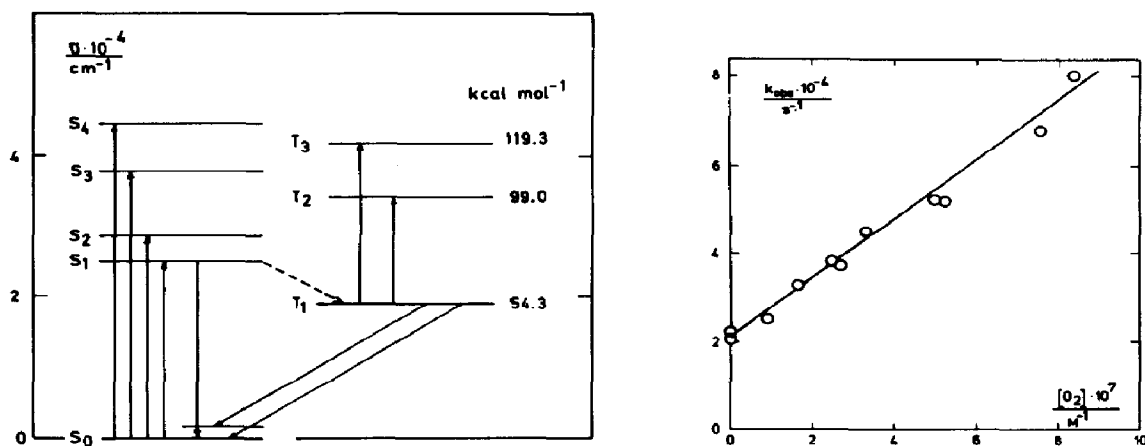


Fig. 7. Energy level diagram for observed transitions in BN.

Fig. 8. Quenching of the triplet state of BN in spectroscopic ethanol by oxygen.

generating singlet oxygen by energy transfer from the triplet of BN to molecular oxygen rather than controlled by the diffusion in a collision process. The stability of the system to photolysis in the presence of oxygen reported above points to a subsequent physical deactivation of the singlet oxygen in ethanol.

The quenching of the triplet state of BN by oxygen was found to be more complex in THF. An increase in the rate of disappearance of the triplet was observed upon photolysis after the addition of a known amount of oxygen. When the solution was repeatedly photolysed, the rate progressively decreased. After only a few flashes the limiting value approached that found in the absence of oxygen, indicating an efficient removal of oxygen. In addition, a permanent decrease in the concentration of BN of about 1% per flash was obtained after flashing which is of the same order of magnitude as that in the absence of oxygen. It is probable that the presence and reactivity of the charge-transfer complex between THF and oxygen (ref. 2, p. 282 and references cited therein) constitutes the major factor controlling the quenching process during photolysis in THF.

Acknowledgments

The author is indebted to Professor Stig Claesson for putting all experimental facilities at his disposal, to Dr. Jan F. Rabek for valuable discussions and finally to Dr. Lars Tegnér for constructive comments on the manuscript.

References

- 1 J. F. Rabek, in C. H. Bamford and C. F. H. Tipper (eds.), *Degradation of Polymers*, Comprehensive Chemical Kinetics, Vol. 14, Elsevier, Amsterdam, p. 425.
- 2 B. Rånby and J. F. Rabek, in *Photodegradation, Photo-oxidation and Photo-stabilization of Polymers*, Wiley, London, 1975.
- 3 J. L. R. Williams, S. Y. Farid, J. C. Doty, R. C. Daly, D. P. Specht, R. Searle, D. G. Borden, H. J. Chang and P. A. Martic, *Pure Appl. Chem.*, 49 (1977) 523.
- 4 V. Y. Kagiya, K. Takemoto, H. Shi and J. F. Rabek, *J. Polym. Sci.*, in the press.
- 5 J. F. Rabek, G. Canbäck and B. Rånby, in preparation.
- 6 S. Claesson, L. Lindqvist and R. L. Strong, *Ark. Kemi*, 22 (1964) 245.
- 7 Landolt-Börnstein, *Zahlenwerte und Funktionen*, Band II, Teil 2, Bandteil b, Springer, Berlin, 1962, pp. 1 - 74.