

PHOTOREACTIONS OF AROMATIC COMPOUNDS—XXVIII¹

PHOTO-INDUCED REACTIONS OF 1-NITROAZULENE AND DERIVATIVES WITH NUCLEOPHILES

C. M. LOK, M. E. DEN BOER, J. CORNELISSE and E. HAVINGA*

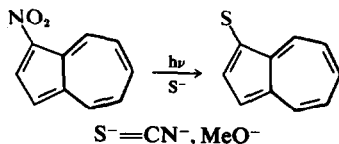
Department of Organic Chemistry, Gorlaeus Laboratories, University of Leiden, P.O. Box 75, Leiden, The Netherlands

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Abstract—The photosubstitutions of azulene, 1-nitroazulene and 3-substituted 1-nitroazulenes with nucleophiles have been investigated. In these azulenes the atom at position 1 proved to be the most reactive in accord with the calculated excited state charge densities. The photomethoxylation of 1-nitroazulene probably proceeds through a triplet state. The quantum efficiency of this reaction proved to be wavelength-dependent indicating that intersystem crossing from higher excited singlet states may occur.

INTRODUCTION

In a previous paper² we reported the photochemical substitution of the nitro group in 1-nitroazulene by cyanide ion and methoxide ion.



The present communication presents a quantitative study of the photoreaction of 1-nitroazulene with methoxide ion (quantum efficiencies, sensitization and quenching experiments) and an investigation into the effect of substituents on the reaction course.

RESULTS

Quantum efficiencies. Quantum efficiencies of the photochemical reaction of 1-nitroazulene with methoxide ion were determined at various wavelengths. The solutions, in MeOH, were 3×10^{-5} M in 1-nitroazulene and 1 M in MeONa. The concentrations of 1-nitro- and 1-methoxyazulene were determined spectrophotometrically. Light intensities were measured by means of potassium ferrioxalate actinometry^{3,4} and corrections applied for the internal filter effect. The results are presented in Table 1.

The ultraviolet and visible absorption spectra at different intervals during the irradiation of 1-nitroazulene in 1 M MeONa in MeOH are in Fig 1.

It has been found⁵ that 1-nitroazulene derivatives in their electronic ground states in solution form complexes with methoxide ion. These complexes do not give rise to substitution products on irradiation

Table 1. Quantum efficiencies of the photoreaction of 1-nitroazulene with methoxide ion (1 M) in methanol at various wavelengths

λ in nm	ϕ
546	< 0.0010
405	0.0020
366	0.0020
313	0.0034
254	0.004

(*vide infra*). Since 1-nitroazulene in MeOH with NaOMe has a molar extinction coefficient different from that in pure MeOH, the possibility of complex formation must be taken into consideration and the quantum yields may need correction for the amount of unproductive light absorbed by the complex.

Unfortunately, neither the extent of complex formation nor the extinction coefficients of a possible complex are known. However, from the extinction coefficients at 405 and 313 nm of 1-nitroazulene in MeOH and in MeOH/MeONa (Table 2), relative corrections can be calculated for the quantum efficiencies at these wavelengths.

If α = the degree of complex formation, the corrected quantum efficiency at 405 nm becomes:

$$\phi_{\text{corr.}}^{405} = \frac{\epsilon'_{405}}{(1-\alpha)\epsilon_{405}} \times \phi_{\text{obsd.}}^{405} = \frac{0.0022}{1-\alpha}$$

whereas the value at 313 nm becomes:

$$\phi_{\text{corr.}}^{313} = \frac{\epsilon'_{313}}{(1-\alpha)\epsilon_{313}} \times \phi_{\text{obsd.}}^{313} = \frac{0.0033}{1-\alpha}$$

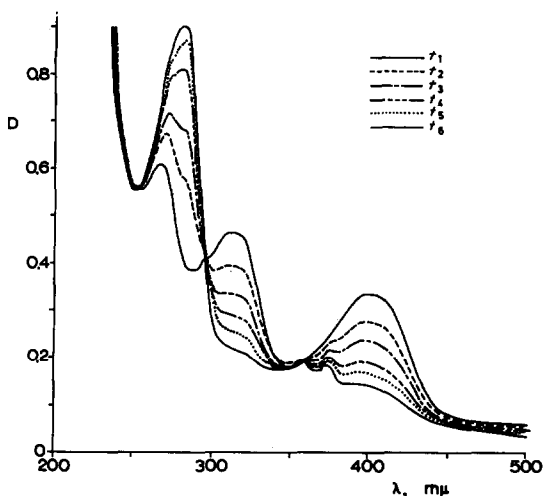


Fig 1. Ultraviolet and visible absorption spectra at different intervals during the irradiation of 1-nitroazulene in 1 M MeONa in MeOH.

Table 2. Molar extinction coefficients of 1-nitroazulene in MeOH (ϵ) and in 1 M MeONa/MeOH (ϵ').

λ in nm	ϵ in CH ₃ OH	ϵ' in CH ₃ ONa/CH ₃ OH(ϵ')
405	12,300	13,800
313	16,300	15,600

In this calculation it has been assumed that the extinction coefficients of the uncomplexed 1-nitroazulene do not change on going to the more polar medium. Comparison with spectral data in non-polar medium⁶ shows, that the ratio of ϵ_{405} and ϵ_{313} increases with increasing solvent polarity enhancing the difference between the corrected quantum efficiencies at 313 and 405 nm.

It follows that the dependence of the quantum efficiency on the wavelength of the exciting light is real and cannot be explained by the presence of complexes in the irradiated solutions.

For 1-cyano-3-nitroazulene in MeONa/MeOH the degree of complex formation and the extinction coefficients of the complex can be determined spectrophotometrically, and the corrected values can be calculated for the quantum yields at 313 and 405 nm. In 0.01 M MeONa solution the values are 9×10^{-4} and 8×10^{-5} , respectively demonstrating a strong variation of the quantum yield with wavelength.

Sensitization. The energy of the lowest triplet state of 1-nitroazulene is not known. One may expect the triplet (like that of azulene, $E_T = 30$ kcal/mole⁷) to be low, possibly < 40 kcal/mole. It was attempted to sensitize the photoreaction with low-energy sensitizers like crystal violet and eosin. These compounds, however, react with methoxide ion.

2-Acetonaphthone ($E_T = 59$ kcal/mole) and 2-naphthylphenyl ketone ($E_T = 60$ kcal/mole) were found to be efficient sensitizers for the disappearance of 1-nitroazulene. The measured rate of formation of 1-methoxyazulene, however, appeared to be much lower than the reaction rate of 1-nitroazulene. This may be caused by photosensitized decomposition of the product, which is photochemically unstable. Moreover, since the energy of the first excited singlet state of 1-nitroazulene is lower than that of the sensitizers, singlet energy transfer cannot be excluded. The results obtained in the experiments with these sensitizers do not provide conclusive evidence concerning the nature of the reacting excited state.

With azulene, which has a lower lying excited singlet than 1-nitroazulene, the reaction could not be photosensitized, possibly because its triplet energy is lower than that of the nitro compound.

Quenching. Compounds with low triplet energies such as perylene ($E_T = 35.6$ kcal/mole) and tetracene ($E_T = 29$ kcal/mole) cannot be used as quenchers because of their high extinction coefficients in the region of the absorption maxima of 1-nitroazulene. Azulene not having this disadvantage proved to be an efficient quencher. However, since its first excited singlet has a lower energy than that of azulene, singlet energy transfer may have taken place.

3,3,4,4-Tetramethyldiazetidine dioxide⁸ has excellent properties as a quencher since it has a low triplet and a high singlet energy ($E_T = 35$ kcal/mole;⁹ $E_S > 85$ kcal/mole). The photoreaction of 1-nitroazulene with methoxide ion could be quenched with this compound. Quantum efficiencies at 405 nm were measured at different quencher concentrations. A plot of the reciprocal of the quantum efficiency versus the quencher concentration is depicted in Fig 2. The straight line satisfies the equation $1/\phi = 625 + 2.73 \times 10^4[Q]$.

Substituted nitroazulenes. Certain 1-nitroazulenes substituted at carbon atom 3 undergo photo-substitution reactions on irradiation in the presence of methoxide ion. The substituent may be Z = NO₂, COCF₃, COCH₃, CHO or CN. The main products of the reaction are 1-methoxy-3-Z-azulene (I) and 1,6-dimethoxy-3-Z-azulene(II). Product yields and reaction conditions are summarized in Table 4 (Experimental Part).

Irradiation of the products of type I did not give rise to formation of products II. The compounds of type II might be formed *via* 6-methoxy-1-nitro-3-Z-azulene by two consecutive photochemical reactions, since the 1-methoxy-3-Z-azulenes are not reactive towards methoxide ion. In the case of 1-nitro-3-trifluoroacetylazulene a third product could be isolated, formed by substitution of the trifluoromethyl group by a methoxy group.

Illumination of 1-nitro-3-Z-azulenes in which Z = Cl, Br, OMe or Me did not afford products of

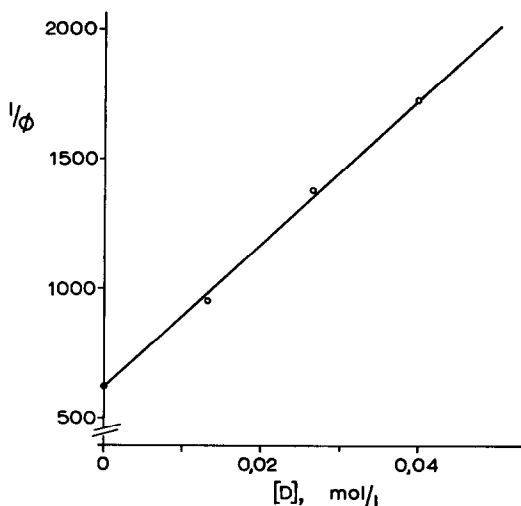
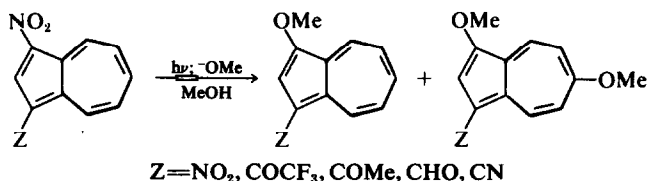


Fig 2. Reciprocal of quantum efficiency at 405 nm of photomethoxylation of 1-nitroazulene versus concentration of 3,3,4,4-tetramethyldiazetidine dioxide.

the types I or II. On prolonged irradiation of 1-chloro- and 1-bromo-3-nitroazulene products were formed in which there is a negative charge on the azulene nucleus as could be deduced from electrophoresis experiments. These products were not further identified.

At high NaOMe concentrations, 1-nitroazulenes with electron withdrawing substituents at position 3 form ground state complexes with methoxide ion.⁵ For this reason, the irradiation experiments had to be carried out at low methoxide ion concentrations. Neither thermally nor photochemically do these complexes give rise to substitution products.

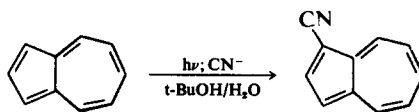
1-Nitro-4,6,8-trimethylazulene, 1,3-dinitro-4,6,8-trimethylazulene and 3-nitroguaiazulene, in which the nitro groups are sterically hindered, do not undergo photosubstitution reactions with methoxide ion.

On the basis of calculated charge densities in the lowest excited singlet and triplet states of azulene¹⁰ also carbon atom 5 is expected to be reactive towards nucleophilic attack, albeit to a lesser extent than carbon atom 1. We irradiated a solution of 1,3-ditert-butyl-5-nitroazulene in 0.1 M NaOMe in

*Later experiments showed that upon irradiation of 1,3-ditert-butylazulene in the presence of cyanide ion 5-cyano-1,3-ditert-butylazulene was formed in low yield.

MeOH (5-nitro substituted azulenes can only be obtained by nitration of azulenes in which the positions 1 and 3 are occupied by electron donating groups). Even upon irradiation for several days, no reaction was observed.*

Other azulene derivatives and azulene itself. Irradiation of 244 mg of azulene in 1500 ml of tert-butyl alcohol/water (2:3) in the presence of 0.1 M KCN for 120 hr in a Rayonet photochemical reactor (3000 Å lamps) afforded 24 mg of 1-cyanoazulene and 182 mg of starting material.



Attempts to establish whether 1-chloro-, 1-bromo-1-methoxyazulene and 1-azulylbenzoate can undergo photosubstitution by cyanide ion failed, because these compounds are thermally too unstable to stand prolonged irradiation as would seem necessary in view of the results obtained with azulene itself. Irradiation of 1-chloro- and 1-bromoazulene in MeOH did not lead to the formation of azulene by homolytic fission of the carbon-halogen bond, a process which is known to occur in the corresponding naphthalene and benzene derivatives.^{12,13}

DISCUSSION

Pariser¹⁰ calculated charge densities of the azulene molecule in the ground state and several excited singlet and triplet states. Table 3 presents the values for the ground state (S_0), the lowest excited singlet state (S_1) and the lowest triplet state (T_1).

The change of the charge densities upon going to the first excited singlet or the first triplet state is in agreement with the results of thermal and photochemical substitution experiments.

Electrophilic substitution (e.g. nitration⁶) in the

Table 3. Calculated charge densities for the ground state (S_0), the lowest excited singlet state (S_1), and the lowest triplet state (T_1) of azulene¹⁰

atom no.	S_0	S_1	T_1
1,3	-0.096	+0.145	+0.138
2	+0.021	-0.118	-0.126
4,8	+0.122	-0.080	-0.067
5,7	-0.049	+0.072	+0.092
6	+0.052	-0.108	+0.128

ground state takes place at carbon atom 1. If the carbon atoms 1 and 3 bear substituents, electrophiles tend to attack at positions 5 (e.g. in the nitration of 1,3-ditert-butylazulene¹⁴). Only two examples of nucleophilic substitution in the ground state of azulene are reported. Reaction with sodium amide leads to 4-aminoazulene,^{15,16} whereas with MeLi azulene is converted, *via* a dihydro compound, into 4-methylazulene.¹⁷

The photocyanation of azulene is to our knowledge the first example reported of substitution of azulene in the excited state. That in this process the nucleophile attaches itself to carbon atom 1 is in accord with the calculated excited state charge densities.*

Calculation of charge densities for the first excited singlet state of 1-nitroazulene¹⁸ shows that carbon atoms 1 and 3 are still bearing the highest positive charges (C1: +0.088; C3: +0.146). If, like in azulene, the charge distribution in the triplet state does not differ substantially from that in the excited singlet state, it is comprehensible that photocyanation of 1-nitroazulene (proceeding *via* the triplet state, *vide infra*) leads to 1-cyanoazulene at a faster rate (due to the better leaving group tendency of the nitro group) than in the case of azulene.

The photoreaction of 1-nitroazulene with cyanide ion, being accompanied by thermal side reactions proved to be less suitable for mechanistic studies than that with methoxide ion. For this reason, the latter nucleophile was chosen as reagent for quantum yield measurements and energy transfer experiments.

The results obtained in the quenching experiments point to a triplet state as a reacting intermediate in the photomethoxylation of 1-nitroazulene. From the Stern-Volmer plot (Fig 2) the value of $k_q\tau$ can be calculated in which k_q is the quenching rate constant and τ is the lifetime of the excited state in the absence of quencher: $k_q\tau = 43.7$ l/mole. If quenching is diffusion-controlled, k_q can be obtained from the Debye-equation:

$$k_q = \frac{8RT}{3000\eta}$$

The viscosity of a 1 M solution of NaOMe in MeOH was determined to be 0.01455 poise.† The calculated lifetime of the 1-nitroazulene triplet is

*Irradiation of naphthalene where positions 1 and 2 bear the same charge in the ground and excited states, in KCN aq was found to afford 1-cyanonaphthalene as the main substitution product.¹¹ In this case and therefore perhaps also in the case of azulene other factors must be position determining.

†Viscosity determinations were made by Mr. H. Schalkers of the Department of Physical Chemistry of this Institute.

thus found to be 10 ns. In view of the relatively short lifetime of the azulene triplet⁷ and the lifetime-shortening influence of the nitrogroup¹⁹ this seems to be a reasonable value. The occurrence of the wavelength dependence of the quantum yield indicates the possibility of intersystem crossing from higher excited singlet states. The observation that the fluorescence of 1-nitroazulene is also found to be wavelength dependent²⁰ supports this view. According to Li and Lim²¹ the occurrence of significant intersystem crossing from higher excited singlet states may be a phenomenon not very uncommon to molecules containing non-bonding electrons. It has been suggested that this effect is responsible for the dependence on the wavelength of the excited light of the phosphorescence of phthalazine²¹ and of Michler's ketone.²²

EXPERIMENTAL

M.ps are uncorrected. IR spectra were taken on a Beckman IR-10 spectrometer. PMR spectra were obtained on a Jeol JNM-PS-100, a Varian A-60 and a Varian HA-100. UV spectra were taken with a Cary 15 spectrophotometer. Mass spectra were obtained on a GEC AEI-MS 902 mass spectrometer.

Quantum yield measurements. For the determination of the quantum yields dilute solutions (2×10^{-5} M) were employed. Monochromatic light was obtained with a Bausch and Lomb High Intensity Monochromator and a SH100 W Hanovia high pressure mercury lamp or with a Bausch and Lomb 500 mm Monochromator and an SP500 or SP 1000 W Philips super high pressure mercury arc.

Materials. Solutions of MeONa in MeOH were prepared by addition of NaH (Fluka A.G., Buchs S.G., Switzerland) to MeOH (p.a. quality from E. Merck, Darmstadt).

1-Chloro-3-nitroazulene and 1-bromo-3-nitroazulene were prepared by halogenation of 1-nitroazulene with N-chloro(bromo)-succinimide in benzene.^{6,23} 1-Nitroazulene and 1,3-dinitroazulene were prepared by nitration of azulene with cupric nitrate in Ac₂O^{6,24} followed by fractional recrystallisation from CH₂Cl₂.

1-Nitro-trifluoroacetylazulene, 1-acetyl-3-nitroazulene, 1-cyano-3-nitroazulene, 3-nitroazulenealdehyde-1,1-methyl-3-nitroazulene and 1-benzoyloxy-3-nitroazulene were prepared by nitration⁶ with cupric nitrate in Ac₂O of the corresponding azulene derivatives.^{25,6,26,27,28,29}

1-Methoxy-3-nitroazulene was prepared by cleavage by base of 1-benzoyloxy-3-nitroazulene in DMF in the presence of MeI.³⁰

1-Nitro-3-trifluoroacetylazulene. m.p. 173–174°; IR (KBr): 1665 cm⁻¹ (CO); UV (MeOH): $\lambda_{\max} = 304, 322, 387, 466$ nm; PMR (CDCl₃, PS-100): $\delta = 10.10$ ppm (dd, 1H, H4), $\delta = 9.97$ ppm (dd, 1H, H8), $\delta = 9.04$ ppm (q, 1H, H2), $\delta = 7.9$ – 8.4 ppm (m, 3H, H5, 6,7).

3-Nitroazulenealdehyde-1. m.p. 221°; IR (KBr): 1662 cm⁻¹ (CO); UV (MeOH): $\lambda_{\max} = 297, 330, 376, 470$ nm.

1-Methoxy-3-nitroazulene. UV (MeOH): $\lambda_{\max} = 333, 450, 580$ nm; PMR (CDCl₃, HA-100): $\delta = 9.65$ ppm (dd, 1H, H4), $\delta = 8.59$ ppm (dd, 1H, H8), $\delta = 7.80$ ppm (s, 1H, H₂), $\delta = 7.3$ – 8.1 ppm (m, 3H, H5, 6,7), $\delta = 4.05$ ppm (s, 3H, OMe).

1-Cyano-3-nitroazulene. m.p. 267–268°; IR (KBr): 2210 cm⁻¹ (CN); UV (MeOH): $\lambda_{\max} = 281, 307, 380,$

Table 4. Irradiation of 1-nitro-3-Z-azulenes in 220 ml MeONa/MeOH. Light source: Hanau TQ 81 mercury arc

Z	amount starting material (mg)	[MeO ⁻]	time of irradiation (min)	1-methoxy-3-Z-azulene (mg)	1,6-dimethoxy 3-Z-azulene (mg)
NO ₂	34	0.003	330	5.4	3.3
COCF ₃	65	0.005	650	4.2	2.0*
CN	25	0.05	150	9.0	2.0
CHO	15	0.1	180	8.5	—
COMe	2.0	0.1	70	1.0	—

* Also 0.9 mg 1-methoxycarbonyl-3-nitroazulene was isolated.

495 nm; PMR (CDCl₃, PS-100): δ = 10.04 ppm (dd, 1H, H4), δ = 8.96 ppm (dd, 1H, H8), δ = 8.80 ppm (s, 1H, H2), δ = 7.9–8.3 ppm (m, 3H, H5, 6, 7).

1-Acetyl-3-nitroazulene. IR (KBr): 1650 cm⁻¹ (CO); UV (MeOH): λ_{\max} = 296, 325, 392, 470 nm.

1-Methyl-3-nitroazulene. UV (MeOH): λ_{\max} = 320, 412, 533 nm; PMR (CDCl₃, A-60): δ = 9.67 ppm (dd, 1H, H4), δ = 8.47 ppm (dd, 1H, H8), δ = 8.23 ppm (s, 1H, H2), δ = 7.4–8.1 ppm (m, 3H, H5, 6, 7), δ = 2.63 ppm (s, 3H, Me).

Procedure of irradiations. Preliminary experiments were performed with dilute (ca. 10⁻⁵ M) solutions in spectrophotometer cells. For preparative scale irradiations a Rayonet Photochemical Reactor type RPR-208 or a Hanau TQ 81 mercury arc (pyrex filter) were used. Upon completion of the irradiation of 3-substituted 1-nitroazulenes in the presence of methoxide ion the volume of the solution was reduced by evaporation of most of the solvent. Upon addition of 100 ml water and 40 g NaCl the solution was extracted (3 \times) with CH₂Cl₂ and the organic layer dried (CaSO₄). After filtration the solvent was evaporated. The residue was subjected to column chromatography on aluminium oxide and eluted with CH₂Cl₂. The product of the photoreaction of azulene with cyanide ion was isolated in a similar procedure but the volume of the irradiation mixture was not reduced and no water was added. Further experimental details are in Table 4.

Identification of irradiation products. 1-Cyano- and 1-methoxyazulene were identified by comparing their UV and PMR spectra with literature and by means of their IR and mass spectra.

1-Methoxy-3-trifluoroacetylazulene. IR (KBr): 1640 cm⁻¹ (CO); UV (CH₂Cl₂): λ_{\max} = 283, 333, 456, 590 nm; PMR (CDCl₃, A-60): δ = 9.74 ppm (dd, 1H, H4), δ = 8.57 ppm (dd, 1H, H8), δ = 7.70 ppm (m, 1H, H2), δ = 7.4–8.1 ppm (m, 3H, H5, 6, 7), δ = 4.10 ppm (s, 3H, OMe); *m/e* (parent peak) = 254.

1-Cyano-3-methoxyazulene. m.p. 82–83°; IR (KBr): 2190 cm⁻¹ (CN); λ_{\max} = 296, 307, 312, 378, 396, 640 nm; PMR (CDCl₃, PS-100): δ = 8.44 ppm (dd, 2H, H4, 8), δ = 7.46 ppm (s, 1H, H2), δ = 7.69 ppm (t, 1H, H6), δ = 7.21 ppm (t, 2H, H5, 7), δ = 4.05 ppm (s, 3H, OMe).

3-Methoxyazulenealdehyde-1. IR (KBr): 1635 cm⁻¹ (CO); UV (CH₂Cl₂): λ_{\max} = 280, 312, 322, 416, 607 nm; PMR (CDCl₃, A-60): δ = 9.28 ppm (dd, 1H, H8), δ = 8.50 ppm (dd, 1H, H4), δ = 7.71 ppm (s, 1H, H2), δ = 7.3–8.1 ppm (m, 3H, H5, 6, 7), δ = 4.06 ppm (s, 3H, OMe), δ = 10.38 ppm (s, 1H, CHO).

1-Acetyl-3-methoxyazulene. IR (KBr): 1635 cm⁻¹ (CO); UV (CH₂Cl₂): λ_{\max} = 275, 305, 316, 408, 422, 630 nm.

1,6-Dimethoxy-3-trifluoroacetylazulene. IR (KBr): 1620, 1631 cm⁻¹ (CO); UV (CH₂Cl₂): λ_{\max} = 290, 346, 456, 545 nm; PMR (CDCl₃, PS-100): δ = 9.62 ppm (d, 1H, H4), δ = 8.42 ppm (d, 1H, H8), δ = 7.38 ppm (m, 1H, H2), δ = 4.01 ppm (s, 3H, OMe), δ = 4.03 ppm (s, 3H, OMe); *m/e* (parent peak) = 284.

1-Cyano-3,6-dimethoxyazulene. IR (KBr): 2190 cm⁻¹ (CN); UV (CH₂Cl₂): λ_{\max} = 306, 314, 320, 378, 400, 596 nm; PMR (CDCl₃, PS-100): δ = 8.30 ppm (d, 2H, H4, 8), δ = 7.18 ppm (s, 1H, H2), δ = 4.00 ppm (s, 3H, OMe), δ = 4.01 ppm (s, 3H, OMe).

1,6-Dimethoxy-3-nitroazulene. UV (CH₂Cl₂): λ_{\max} = 298, 354, 465 nm; PMR (CDCl₃, PS-100): δ = 9.51 ppm (d, 1H, H4), δ = 8.45 ppm (d, 1H, H8), δ = 7.49 ppm (s, 1H, H2), δ = 4.04 ppm (s, 3H, OMe), δ = 4.03 ppm (s, 3H, OMe).

1-Methoxycarbonyl-3-nitroazulene. IR (KBr): 1700, 1716 cm⁻¹ (CO); UV (CHCl₃): λ_{\max} = 289, 312, 390, 465 nm; PMR (CDCl₃, PS-100): δ = 9.96 ppm (dd, 1H, H4), δ = 9.85 ppm (dd, 1H, H8), δ = 8.96 ppm (s, 1H, H2), δ = 7.7–8.1 ppm (m, 3H, H5, 6, 7), δ = 4.00 ppm (s, 3H, OMe); *m/e* (parent peak) = 231.

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REFERENCES

- Part XXVII, G. Lodder and E. Havinga, *Tetrahedron*, **28**, 5583 (1972).
- C. M. Lok, J. Lugtenburg, J. Cornelisse and E. Havinga, *Tetrahedron Letters* 4701 (1970).
- C. A. Parker, *Proc. Roy. Soc. A220*, 104 (1953).
- C. G. Hatchard and C. A. Parker, *Ibid.* A235, 518 (1956).
- C. M. Lok, Maria E. den Boer and J. Cornelisse, *Rec. Trav. Chim.*, to be published.
- A. G. Anderson, J. A. Nelson and J. J. Tazuma, *J. Am. Chem. Soc.* **75**, 4980 (1953).
- P. M. Rentzepis, *Chem. Phys. Letters* **3**, 717 (1969).
- P. Singh, D. G. B. Boocock and E. F. Ullman, *Tetrahedron Letters* 3935 (1971).
- E. F. Ullman, personal communication to J. Lugtenburg.
- R. Pariser, *J. Chem. Phys.* **25**, 1112 (1956).
- J. A. J. Vink, C. M. Lok, J. Cornelisse and E. Havinga, *Chem. Comm.* 710 (1972).
- J. T. Pinhey and R. D. G. Rigby, *Tetrahedron Letters* 1267 (1969).
- C. M. Lok, unpublished results.

- ¹⁴K. Hafner and K. L. Moritz, *Ann.* **656**, 40 (1962).
¹⁵D. H. Reid, W. H. Stafford and J. P. Ward, *J. Chem. Soc.* 1100 (1958).
¹⁶A. G. Anderson, D. J. Gale, R. N. McDonald, R. G. Anderson and R. C. Rhodes, *J. Org. Chem.* **29**, 1373 (1964).
¹⁷K. Hafner and H. Weldes, *Ann.* **606**, 90 (1957).
¹⁸C. M. Lok, Dissertation, Leiden (1972).
¹⁹R. Rusakowicz and A. C. Testa, *Spectrochim. Acta* **27A**, 787 (1971).
²⁰R. C. Dhingra and J. A. Poole, *Chem. Phys. Letters* **2**, 108 (1968).
²¹Y. H. Li and E. C. Lim, *J. Chem. Phys.* **56**, 1004 (1972).
²²W. Klöpffer, *Chem. Phys. Letters* **11**, 482 (1971).
²³A. G. Anderson and R. N. McDonald, *J. Am. Chem. Soc.* **81**, 5669 (1959).
²⁴A. G. Anderson, R. Scotoni, E. J. Cowles and C. G. Fritz, *J. Org. Chem.* **22**, 1193 (1957).
²⁵A. G. Anderson and R. G. Anderson, *Ibid.* **27**, 3578 (1962).
²⁶W. Treibs, J. Hiebsch and H. J. Neupert, *Chem. Ber.* **92**, 606 (1959).
²⁷K. Hafner and C. Bernhard, *Angew. Chem.* **69**, 533 (1957).
²⁸K. Hafner, *Ann.* **606**, 79 (1957).
²⁹A. G. Anderson and G. M. C. Chang, *J. Org. Chem.* **23**, 151 (1958).
³⁰L. L. Replogle, *Ibid.* **29**, 2805 (1964).