and the water-insoluble di-*o*-tolylurea, m.p. 270° dec. The infrared spectrum of the isolated urea was identical with that of an authentic sample.

Reaction of Ic with Ammonia.—A 3.2-g. sample (0.01 mole) of Ic was added to methanolic ammonia. When the solvent was evaporated, the hydrochloride of N,N′-di-*o*-tolylguanidine was obtained. From this, on treatment with aqueous sodium hydroxide, was isolated di-*o*-tolylguanidine (III), m.p. 183–185° (lit., m.p. 179°). A solution of 1 g. of di-*o*-tolylcarbodiimide in 10 ml. of benzene was saturated with ammonia in the presence of 10 mg. of cupric chloride to give 74.5% of III, m.p. 186–187°. No depression of the melting point was caused when samples of III prepared by the above methods were mixed. The infrared spectrum was identical with that of an authentic sample.

Reaction of Ic with Hydrazine Hydrate.—A 2.2-g. sample (0.007 mole) of Ic was added to 1.44 g. (0.03 mole) hydrazine hydrate in a mixture of 20 ml. of tetrahydrofuran and 20 ml. of water. An immediate reaction took place. After the mixture had been stirred, with ice-cooling, 1.4 g. (73%) of 3-*o*-tolylamino-5-hydroxy-4-*o*-tolyl-1,2,4,4H-triazole (IV) had separated. It crystallized from benzene in white crystals, m.p. 198–199°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ (infrared): 2.96, 3.20, 3.30–3.40, 5.84, 6.17, 6.28, 6.48, 6.84, 7.27, 7.62, and 11.61 μ.

Anal. Calcd. for $C_{16}H_{16}N_4O$: C, 68.55; H, 5.75, N, 19.99. Found: C, 68.72; H, 5.96; N, 19.92.

In a similar experiment, using benzene as the solvent, IV was obtained in 83% yield. IV is soluble in dilute sodium hydroxide and it could be reprecipitated by acid.

Acknowledgment.—The authors wish to thank Mr. B. Tucker for his valuable help with the experiments and Mr. F. Geremia for the determination of numerous infrared spectra.

The Structure of Nidulin

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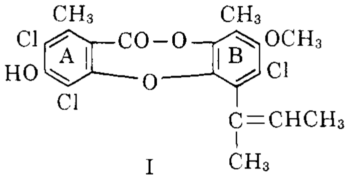
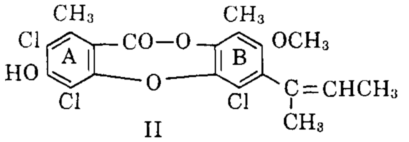
Nidulin,[1] the chief chlorine-containing metabolite of a non-ascosporic strain of *Aspergillus nidulans*, has been allocated[2,3] structure I. Shortly after the publication of our last paper,[3] Beach and Richards claimed[4] that nidulin should be represented by structure II. Although we still maintain that the evidence which we have already presented[2,3] is sufficient to establish the correctness of our structure, we present the following additional arguments in favor of structure I.



I



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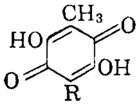
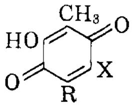
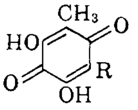


III



IV



V

a. R = —C(CH$_3$)=CHCH$_3$
b. R = —CH(CH$_3$)$_2$

Degradation of nidulin under strictly defined conditions[3] yielded nucleus B as a dihydroxybenzoquinone which we have formulated,[3] on the basis of analysis, color reactions, and ultraviolet absorption spectrum,[5] as IIIa. If nidulin had possessed structure II, then the degradation product would have had structure Va. We have now compared (see Table I) the ultraviolet and infrared absorption spectra of the degradation product IIIa with the corresponding spectra of dihydroxythymoquinone[6] (IIIb) and of 3,5-dihydroxy-2,6-dimethylbenzoquinone[7] (V; R = CH$_3$). We also record (see Table I) the spectra of monohydroxythymoquinone[6] (IVb; X = H) and of the chloroquinone (IVa; X = Cl) which is obtainable[3] as a degradation product of nidulin. The three last-mentioned quinones, as expected,[8] show two carbonyl bands in their infrared spectra. (The two bands are not clearly resolved in the solution spectra of the chloroquinone and of 3,5-dihydroxy-2,6-dimethylbenzoquinone.)

Information from the ultraviolet absorption spectra does not differentiate clearly between the two possibilities for the nidulin degradation product (IIIa or Va). However, the evidence from the infrared absorption spectra establishes unequivocally that the degradation product has structure IIIa. Hence the chloroquinone has structure IVa (X = Cl). We maintain, therefore, that nidulin is correctly represented by structure I.

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Table I

Compound	Ultraviolet absorption spectrum^a (EtOH), $\lambda_{\max}$ in mμ (log ϵ)	Infrared absorption spectrum^b (O—H and C=O stretching vibrations), $\nu_{\max}$ in cm.$^{-1}$ Disk (KBr)	Solution (CHCl$_3$)
IIIa	287 (4.24), 436 (2.40)	3310, 1617	3365, 1642
IIIb	293 (4.31), 435 (2.36)	3319, 1616	3327, 1640^c
IVb (X = H)	267 (4.16), 404 (3.01)	3252, 1668, and 1643	3431, 1662, and 1645
IVa (X = Cl)	278 (4.15), 334 (3.24) 405 (2.77)^d	3411, 1665, and 1655	3431, 1662, and 1654^d
V (R = CH$_3$)	297 (4.26), 426 (2.26)	3417, 1660, and 1641	3476, 1653, and 1645^d

^{a} Taken on a Unicam S. P. 500. ^{b} Taken on a Unicam S. P. 100. ^{c} Compound IIIb is only sparingly soluble in chloroform. It is more soluble in bromoform and a solution in this solvent showed a single carbonyl peak at 1637 cm.$^{-1}$. ^{d} Shoulder.

Acknowledgment.—We thank Dr. J. H. Richards (personal communication) for drawing our attention to the existence of the quinone V (R = CH_3).

The Anomalous Behavior of *m*-Trifluoromethylnitrosobenzene Dimer[1]

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Contribution No. 244 from the Central Research Laboratories of Minnesota Mining and Manufacturing Company, St. Paul 19, Minnesota

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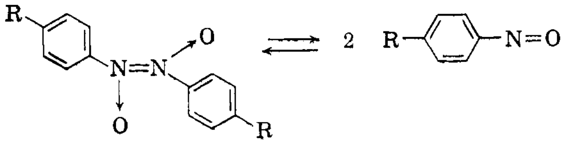
It is well known that most aromatic nitroso compounds exist as colorless or pale yellow dimers in the crystalline state but dissociate to intensely green-colored monomers in the liquid state.[2,3]



para-Substituents such as R_2N—, I, Cl, and CH_3 increase the tendency for dissociation owing to electronic interaction with the aromatic system, thereby weakening the N-N bond.[3] In fact, the effect is so great with *p*-nitrosodimethylaniline and with *p*-iodonitrosobenzene that these compounds are monomeric even in the solid state. When electronic interaction is prevented by *ortho* substituents that preclude formation of a planar configuration, the nitroso molecule exists mostly as a dimer even in solution. Thus, in a 1% benzene solution, nitrosomesitylene is dimerized 77%[4,5] whereas *p*-nitro-, *p*-bromo-, *p*-methylnitrosobenzene, and nitrosobenzene are dimerized less than 4%.[4,5] *m*-Substituents are reported[5] to have little or no effect on the N-N bond.

In view of these generally accepted properties of aromatic nitroso compounds, we wish to report the anomalous stability of the *m*-trifluoromethylnitrosobenzene dimer. This dimer is a white crystalline compound that melts at 48.5–49.0° forming a light amber oil. It dissolves in organic solvents giving water white to light amber solutions. The compound can be distilled at atmospheric pressure (b.p. 295°). The vapor is light green and the distillate when recrystallized from methyl alcohol is obtained as light yellow needles (m.p. 44–46°). Unlike nitrosobenzene dimer, which must be stored in a refrigerator, *m*-trifluoromethylnitrosobenzene dimer is air and light stable at room temperature and can be kept on the shelf for at least ten years without decomposition. This nitroso compound could not be reoxidized to the nitro compound using potassium permanganate in acetone, potassium dichromate in sulfuric acid, or hydrogen peroxide in acetic acid. Neither could it be reduced with ferrous ammonium sulfate in aqueous hydroxide. Much stronger reducing systems such as zinc or tin in aqueous hydrochloric acid were required for reduction to the corresponding amine.

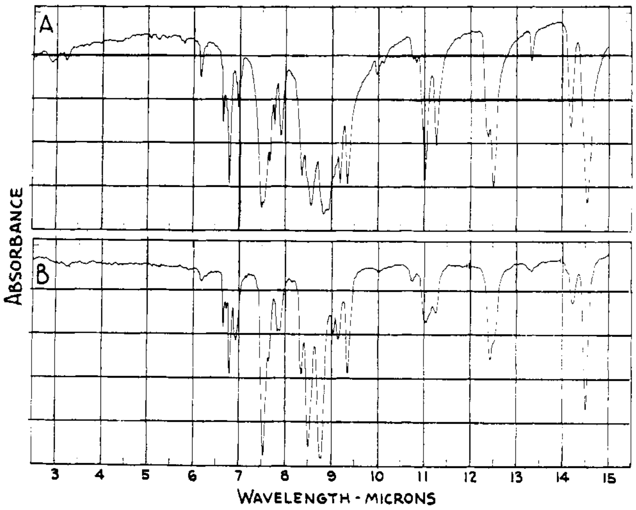


Fig. 1.—Infrared spectra of *m*-trifluoromethylnitrosobenzene dimer (A) in potassium bromide mull and (B) in carbon tetrachloride solution, 3–12 μ and 14–15 μ; in carbon bisulfide solution, 12–14 μ.

The empirical formula for *m*-trifluoromethylnitrosobenzene was established by elemental analysis. The molecular weight was determined cryoscopically using naphthalene and ebulloscopically using benzene. Both methods indicated that the compound was a dimer. The infrared spectra of this compound in its crystalline state and in solution are very similar as shown in Fig. 1, supporting the premise that no dissociation occurs at room temperature in solution. The ultraviolet absorption spectrum in ethanol [0.21 g./l.; peaks at 3150 Å., ϵ (l./g.-cm.) 42.9; at 2540 Å., ϵ 23.6; at 2320 Å., ϵ 30.8] also showed no evidence for the presence of the monomer. Dissociation in solution, however, begins to occur at temperatures above 100°.

N.m.r. data for this compound, summarized in Table I, are consistent with that anticipated for the symmetrical dimer as represented by the azodioxide structure.

Reduction of the dimer with zinc in aqueous hydrochloric acid gave *m*-trifluoromethylaniline which was identified by infrared analysis, and by conversion to its acetyl derivative.

m-Trifluoromethylnitrosobenzene dimer is prepared easily by reduction of *m*-trifluoromethylnitrobenzene with mild reducing systems such as ethylmercaptan in aqueous alkali, zinc in aqueous ammonium chloride, and even alcoholic sodium hydroxide. The reaction gives a mixture of reductive dimerization products from which the desired azodioxide can be isolated in 30–40% yield as described in Experimental.

Experimental

Reduction with Ethylmercaptan.—Ethylmercaptan (1.2 moles) was added dropwise to a chilled mixture of *m*-trifluoromethylnitrobenzene (0.3 mole), water (400 cc.), and sodium hydroxide

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[1] Part of this work was completed in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Division of the M. W. Kellogg Co. in March, 1957.

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