

Reflection Spectra of *N*-Nitrosodimethylamine and *N*-Nitrosodiethylamine

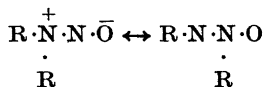
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The extinction coefficients of the two characteristic maxima for *N*-nitrosodimethylamine, DMNA, and *N*-nitrosodiethylamine, DENA, are $E_{M_1} = 3.87$, λ_{max_1} 230 nm,¹ corresponding to a $\pi - \pi^*$ transition,² and E_{M_2} 1.98 λ_{max_2} 332 nm for DMNA and E_{M_2} 1.93 λ_{max_2} 340 nm for DENA. Thus, absorption photometry cannot be applied in studies of very small quantities of the compounds.

Stable systems result after solidifying of even very small amounts of DMNA and DENA dissolved at 50° in liquid cetyl alcohol, m.p. 49°. The solid preparations give excellent reflection spectra. Cetyl alcohol itself has a favourable reflection spectrum (Fig. 1D) as measured against MgO as reference, the spectral reflectivity of which is well known.³ The term reflectivity used in this paper is defined as the reflection coefficient at the wave number $\bar{\nu}$ in question, i.e. the ratio of the intensity of the light reflected from the surface to the intensity of the total incident light of the same wave number. Using a suitably constructed reflection spectrophotometer, reflection spectra of solid cetyl alcohol can be taken from $\bar{\nu}$ 4.61 μm^{-1} (217 nm) to $\bar{\nu}$ 1.43 μm^{-1} (700 nm).

The reflection spectra of DMNA and DENA in solid cetyl alcohol at 20° (Fig. 1, A and B) both have two characteristic minima, one at $\bar{\nu}_1$ 4.15 \pm 0.01 μm^{-1} , 5.15 \pm 0.01 eV, and the other at $\bar{\nu}_2$ 2.85 \pm 0.01 μm^{-1} , 3.53 \pm 0.01 eV, corresponding to the formula



N-Nitrosodialkylamine.

The reflectance, defined as $-^{10}\log$ reflectivity of DMNA or DENA in solid cetyl alcohol, is not strictly proportional to the concentration of DMNA or DENA. Interpolation is only permissible within narrow limits.

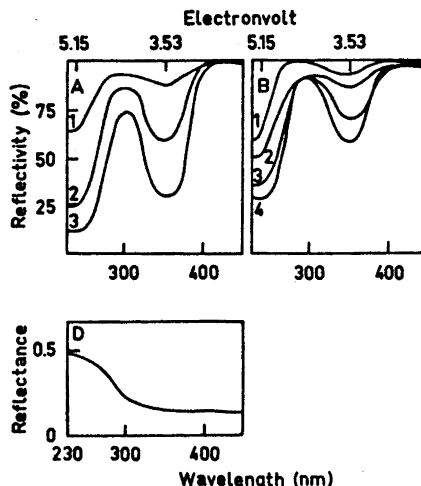


Fig. 1. Reflection spectra of *N*-nitrosodimethylamine, DMNA, and *N*-nitrosodiethylamine, DENA, in solid cetyl alcohol on frosted quartz. Curves A 1, 2, and 3 show the reflectivities of 0.0134, 0.096, and 0.48 $\mu\text{g}/\text{mm}^2$ of DMNA. Curves B 1, 2, 3, and 4 give the reflectivities of 0.030, 0.046, 0.350, and 1.028 $\mu\text{g}/\text{mm}^2$ of DENA. The reflectance of solid cetyl alcohol at 20° is given in D. Measurements in A and B were made with solid cetyl alcohol on frosted quartz as reference. For curve D, by burning of pure Mg freshly prepared MgO on quartz, was used as reference.

Quantities of 1×10^{-8} mol ($\approx 1 \mu\text{g}$) of DMNA or DENA are detected and determined with a mean error of about 5% of value. When very small quantities of DMNA or DENA are studied, a scale expander is suitably connected to the recorder. The recordings given in Fig. 1 were made without expansion.

Experimental. Pure DMNA and DENA were prepared as follows. To 3 g (0.044 mol) of NaNO_2 , analytical grade, and 2.2 g (0.028 mol) of dimethylammonium chloride or 3 g of diethylammonium chloride, analytical grade, dissolved in 10 ml redistilled H_2O , 2 drops of redistilled constant boiling HCl, 1:1 v/v were added. The mixture was heated on a waterbath to 60° for 10 min, allowed to cool slowly and then centrifuged. The nitrosodialkylamine layer was separated off and distilled in a semimicro fractionating apparatus.

The purity was controlled with 0.25 mm silica gel thin-layer chromatograms with dichloromethane, ethyl ether, and hexane 2:3:4 as moving solvent. The R_F -values were 0.23 for DMNA and 0.48 for DENA.

The work with DMNA and DENA must be carried out with the greatest caution. These compounds are extremely potent carcinogens^{1,4} even in very low concentrations. They seem to be a major candidate class of carcinogens that are likely to be causally related to human cancer.⁴

DMNA and DENA are dissolved in liquid, pure cetyl alcohol at 50°. Thin layers, suitable for reflection spectrophotometry are easily prepared by shedding the solution on frosted quartz plates at the same temperature. Depending on the construction of the spectrophotometer used, areas from 5 mm² upwards can be measured. Spectroreflectometers with an integrating sphere, as used in the measurement of the contribution of fluorescence to the brightness of papers treated with whitening agents,⁵ allow a convenient work but require a reflecting area of approximately 315 mm². A suitable layer thickness which always should be kept constant, is 0.2 mm, corresponding to 0.162 mg cetyl alcohol/mm² at 20°, or 51 mg cetyl alcohol on the larger area of 315 mm² of spectroreflectometers with integrating sphere. The measurements reported in this paper were carried out with integrating sphere, using 60 mg cetyl alcohol on 315 mm². The appropriate quantity of cetyl alcohol, and solution of *N*-nitrosodialkylamines in cetyl alcohol, respectively, was applied with an automatic pipette.

A 5" strip chart linear and log potentiometric recorder was used.

1. Druckrey, H., Preussmann, R., Ivankovic, S. and Schmähl, D. *Z. Krebsforsch.* **69** (1967) 103.
2. Kasha, M. *Discussions Faraday Soc.* **9** (1950) 14.
3. Benford, F., Lloyd, G. P. and Schwartz, J. *J. Opt. Soc. Am.* **38** (1948) 445, 964.
4. Lijinsky, W. and Epstein, S. S. *Nature* **225** (1970) 21.
5. Grum, F. and Wightman, T. *Tappi* **43** (1960) 400.

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On Some Kinematic Phenomena in π -Benzene Sandwich Compounds

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In a recent work we have performed¹ a vibrational analysis of dibenzenechromium, $\text{Cr}(\text{C}_6\text{H}_6)_2$, treated as a 25 atomic molecule. In contrast to former partial analyses² the study revealed an interesting kinematic coupling between some ligand and framework normal vibrations. The most striking manifestation of this coupling was observed for the A_{2u} non-planar C-H deformation of benzene. Its frequency is found at 794 cm⁻¹ (IR, in-phase, A_{2u})^{4,5} and at 791 cm⁻¹ (Raman, out-of-phase, A_{1g})² in the spectra of dibenzenechromium (DBC). Its value in free benzene is much lower (671 cm⁻¹).⁶ Consequently, the corresponding force constant for DBC is increased very much (39.7 %) over the free benzene value, if a normal coordinate analysis is executed treating benzene in DBC as an isolated molecule with D_{6h} symmetry.

In marked contrast a total vibrational analysis of DBC as a 25 atomic complex allows a reproduction of the observed A_{2u} frequency by a force constant which is exactly the same as that of free benzene.¹ This astonishing fact is caused by a strong coupling between No. 11 (A_{2u})⁴ and Nos. 23 (A_{2u}) and 21 (A_{1g})^{3,4} in the IR and the Raman spectra, respectively. The reason for this coupling is a nonvanishing off-diagonal element in the corresponding G-matrix block.

In order to check whether the same coupling is also found in other benzene sandwiches, we have executed a total normal coordinate analysis of $\text{Cr}(\text{C}_6\text{H}_6)_2^{+}$, $\text{V}(\text{C}_6\text{H}_6)_2$, $\text{Mo}(\text{C}_6\text{H}_6)_2$, $\text{W}(\text{C}_6\text{H}_6)_2$, $\text{Te}(\text{C}_6\text{H}_6)_2^{+}$ and $\text{Re}(\text{C}_6\text{H}_6)_2^{+}$, using without any additional refinement the same force field and the same structural parameters as in the DBC study.¹ The result for the No. 11 A_{2u}