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Absorption of Cyclic Polynitramines in the Solid and Solvated States

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Earlier work based on specular reflectance measurements on single crystals of the cyclic polynitramine known as RDX indicated the presence of an absorption band near 340 nm. Since a similar band was not observed in dilute solution, the absorption was attributed to the formation of a charge-transfer self-complex in the crystalline state. This work compares measurements of the transmittance of thin single crystals and new specular reflectance measurements to absorption spectra of saturated solutions of the polynitramines known as RDX and HMX. The results are found to support the charge-transfer self-complex hypothesis.

1 INTRODUCTION

The compounds 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) are saturated heterocyclic compounds used as military explosives. The nitro groups, which give these compounds their explosive behavior, are bonded to the ring nitrogen atoms (see Figures 1 and 2). Since the resulting $\rangle N—NO_2$ moiety is called a "nitramine" group, these compounds are sometimes referred to as "cyclic polynitramines." The RDX molecule in solution is a nonplanar six-membered ring which at room temperature undergoes rapid interconversion in which the ring nitrogen atoms oscillate about the planar (sp^2) position.[1] The molecular orbital calculations of Orloff, *et al.*[2] indicate a relatively high positive charge ($q = +0.21$) on the carbon atoms and an even greater negative charge ($q = -0.33$) on the oxygen atoms. The HMX molecule is based on an eight-membered ring whose conformation in solution is not yet known. However, due to the strain expected in such a structure, the ring is almost certainly nonplanar. No molecular orbital calculations are yet available for HMX; however since its optical absorption spectrum is almost identical to

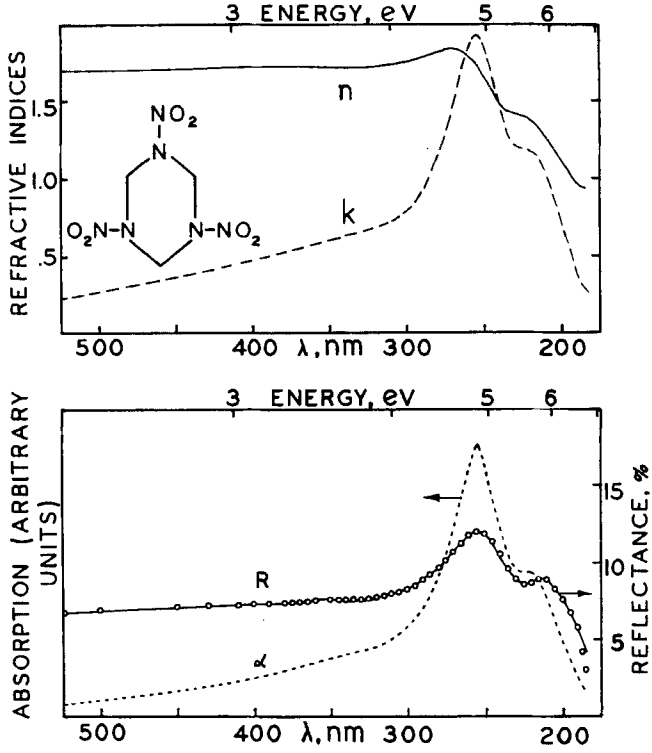

FIGURE 1a (Top) Values of n, the real part (solid line), and k, the imaginary part (dashed line) of the complex index of refraction calculated from the specular reflectance of an RDX single crystal.
1b (Bottom) Values of calculated absorption, α (dotted line), and reflectance, R, for RDX. Open circles are calculated reflectance, and solid line is observed reflectance.

that of RDX,[3] it seems reasonable to assume that conclusions drawn from the RDX calculations are applicable to HMX as well.

The absorption spectrum of RDX in acetonitrile solution consists of two distinct bands at 236 nm (ε = 11,000 L M^{-1} cm^{-1}) and at 195.5 nm (ε = 16,400 L M^{-1} cm^{-1}) with weak vibrational structure superimposed on each band.[2] Orloff, *et al.*, assigned these absorptions primarily to $\pi \rightarrow \pi^*$ transitions localized on the NO_2 groups. In addition they concluded that there were weak $n \rightarrow \pi^*$ absorptions buried in the 236 nm band which result from the promotion of nonbonding electrons on the oxygen atoms. We will refer to this system of overlapping bands as the "nitramine band," since, as pointed out by Stals,[3] the π, n, and σ orbitals are intimately mixed in nitramine type molecules. Orloff, *et al.*, assigned the lowest excited singlet

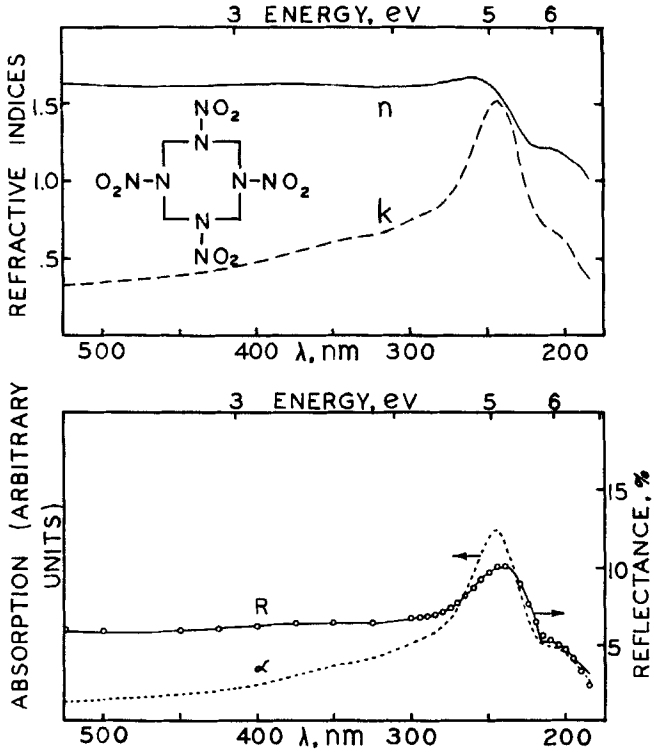

FIGURE 2a (Top) Values of n, the real part (solid line), and k, the imaginary part (dashed line) of the complex index of refraction calculated from the specular reflectance of an HMX single crystal.
2b (Bottom) Values of calculated absorption, α (dotted line), and reflectance, R, for HMX. Open circles are calculated reflectance, and solid line is observed reflectance.

state of RDX to an $n \rightarrow \pi^*$ transition occurring in the long-wavelength tail of the nitramine band.

The crystal structure of RDX has been the subject of a number of studies, the most recent being that of Choi and Prince.[4] There are two known polymorphs, of which only one is stable. This stable form is orthorhombic, with eight molecules per unit cell. Orloff, *et al.*,[2] have remarked on the short C—O constant distances in crystalline RDX, and Stals[5] has concluded that the bonding in the crystal is dominated by electrostatic forces, rather than hydrogen or van der Waals bonding. Choi and Prince[4] also note several contact distances which are shorter than the sum of the van der Waals radii.

HMX can be crystallized in any of four polymorphic forms, the common one, known as β-HMX, being monoclinic, with two molecules per unit cell.

Stals[5] has noted the presence of short C—O distances similar to those observed in RDX. Choi and Boutin,[6] in the latest refinement of the structure by neutron diffraction, conclude that all oxygen atoms on the periphery of the molecule are involved in contacts shorter than the sum of the van der Waals radii. In both materials, it appears that bonding in the solid state is dominated by electrostatic forces, probably by pairing of the highly charged sites on the individual molecules. Such bonding could account for the high heats of sublimation of RDX (31.1 kcal/mol) and HMX (41.9 kcal/mol),[7] and the possibility that it is responsible for a new absorption band in the solid is the subject of this paper.

The specular reflectance measurements of Stals[5] show an absorption band near 340 nm in solid RDX. Based on the fact that this band is observed in the solid and (apparently) not in solution, he attributed it to charge-transfer self-complex formation. However, as will be shown below, the molar absorptivity at 340 nm is only about 0.006% as great as at 195.5 nm, where $\varepsilon = 16{,}400\ \text{L M}^{-1}\ \text{cm}^{-1}$. Thus, any measurement on a solution dilute enough to show the 195.5 nm band is certainly too dilute to display the 340 nm band.

Maycock, *et al.*,[8] have obtained transmission spectra for an HMX single crystal at 77 K which show structure on the absorption tail between 320 and 420 nm. The thickness of the crystal was not given, so that the absorptivity at 340 nm could not be determined. Since these authors found no evidence of this structure in the absorption spectrum of a 0.034 M solution of HMX in acetone, they attributed it to a solid state effect. Again, however, such a solution would be too dilute to allow detection of the 340 nm band.

In an effort to resolve this question, we have repeated these measurements using saturated solutions of RDX and HMX in acetonitrile, and a 10 cm path length. These results are compared to new reflectance and transmission measurements on single crystals.

2 EXPERIMENTAL

The single crystals of RDX and β-HMX used for the reflectance measurements were grown by evaporation of acetone solutions. Starting material was recrystallized a minimum of two times from acetone. The crystals so obtained measured roughly 5 mm along their maximum dimension. Melting points were checked by differential scanning calorimeter. Samples were mounted in a semi-micro reflectance accessory to the Cary 14R spectrophotometer, in which the angle of incidence of the extreme ray is 6°. The as-grown surfaces were used for the reflectance measurements, which were made at 300 K. The double-beam absorbance mode was used, with the

reference beam attenuated by a 0.5 absorbance screen. The reflectance of the sample was compared to that of a front-surface aluminized mirror.

The reflectance data were analyzed by the method described by Verleur.[9] Unlike the Kramers–Kronig technique, this "summation of oscillators" representation works well even in regions of the spectrum where the crystal is transparent. In this method, the complex dielectric constant of the system is represented by a set of classical oscillators. To each oscillator is assigned a frequency, an intensity, and a linewidth. From these parameters, the complex dielectric constant is determined and used to calculate the reflectivity as a function of frequency. The oscillator parameters are then varied by an automatic curve-fitting procedure, until an adequate fit to the measured reflectance spectrum is obtained. The curve-fitting program was written in FORTRAN for the CDC 6600 computer, and was weighted to produce the best fit to the measured reflectance data at the long-wavelength end of the spectrum. A set of six oscillators was used to represent the RDX and HMX spectra in the region 185–550 nm. Oscillators with frequencies outside this interval contribute principally to the baseline. As with other methods of analyzing reflectance data, the difficulty in accurately assigning the zero and 100% reflectance points to the experimental spectrum can lead to large errors in the magnitude of the absorption coefficient, and to baseline shifts. For this reason, the absorption in Figures 1–3 is given in arbitrary units. However, the peak positions and relative intensities are believed accurate. Other possible sources of error are discussed in Reference 9.

The crystal used for the transmission spectrum of HMX was grown by evaporation of an acetonitrile solution. However, the RDX crystal measured in transmission was prepared by sublimation under reduced pressure (40 cm) of argon. Transmission spectra were measured in a Cary Model 14R spectrophotometer at 300 K with polarized light obtained by passing the beam through a Polaroid HNP'B polarizing film. The orientation of the film was fixed relative to the spectrometer, while the crystal was rotated in a special fixture. The absorption of the polarizing film was first measured, and subtracted from subsequent measurements of the film and crystal combination. X-ray diffraction was used to establish the relationship between the polarization direction and the crystallographic axes.

The RDX used in the measurements of solution spectra was recrystallized a minimum of three times from spectrograde acetone. HMX was prepared by nitrolysis of 1,5-diaceto-3,7-dinitro-1,3,5,7-tetraazacyclooctane (known more simply as DADN)[10] and was recrystallized five times from spectrograde acetone. Liquid chromatographic analysis of the product indicates 1-aceto-3,5,7-trinitro-1,3,5,7-tetraazacyclooctane as an impurity in the amount of 0.1%. Absorption spectra were measured using a 10 cm path length; path length for circular dichroism measurements was 1 cm.

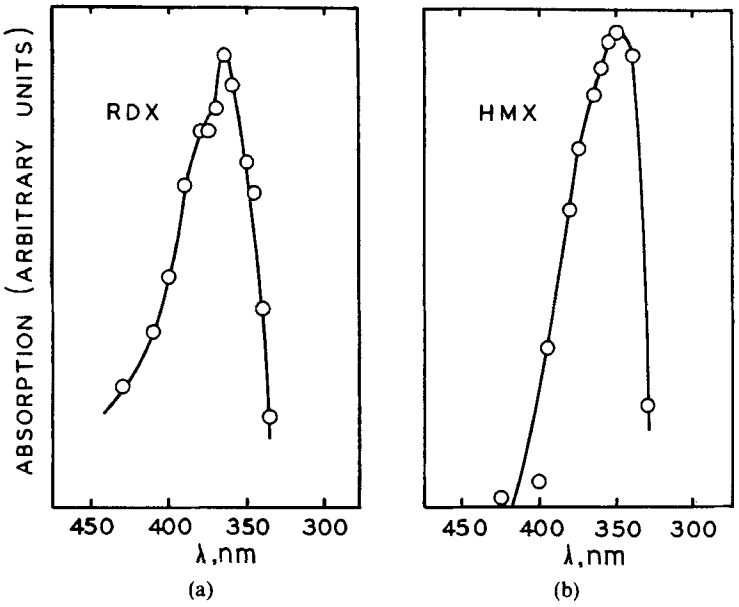

FIGURE 3a (Left) The weak band in solid RDX after subtraction of the tail of the strong nitramine band.
3b (Right) The weak band in solid HMX after subtraction of the tail of the strong nitramine band.

Circular dichroism (CD) spectra of both RDX and HMX in acetonitrile solution were recorded on a Cary Model 60 CD spectrometer. For different wavelength intervals, different concentrations were used to keep the absorption within the limits for optimum sensitivity of the technique.

3 RESULTS

The real and imaginary parts of the complex index of refraction determined from the reflectance measurements are shown in Figure 1a for RDX, and Figure 2a for HMX. The absorption coefficient, α, as well as the calculated and measured reflectance are shown in Figure 1b for RDX, and Figure 2b for HMX. In both cases the strongest band is seen to be the nitramine band, which in the solid occurs at 255 nm in RDX, and 245 nm in HMX. To the short-wavelength side of the nitramine band is a less intense band which occurs at approximately 220 nm in RDX and 202 nm in HMX. The weakest band lies on the long-wavelength tail of the nitramine band, in the vicinity

of 355 nm. It is this band which has no counterpart in the absorption spectra of solvated RDX and HMX.

Urbach's rule predicts that the tails of electronic absorption bands in certain solids follow the expression[11]

$$\alpha(\nu) = \text{Const. } e^{-(\nu - \nu_0)/kT} \tag{1}$$

where ν_0 is the frequency at which the absorption coefficient is maximum for the band in question. Therefore the tabulated data from which Figures 1b and 2b were plotted were graphed as a function of ν on a semilogarithmic plot, and used to obtain an analytical expression having the form of Eqn. (1) for the tail of the nitramine band. This expression was used to calculate values of absorption which were subtracted from the experimentally determined absorption. Figures 3a and 3b show the weak band after subtraction of the tail of the nitramine band. The vertical scale is exaggerated for clarity. In each case there remains a skewed absorption band, peaking at 365 nm in RDX and 350 nm in HMX. There is also a suggestion of slight structure near 380 nm. The absorption drops abruptly to nearly zero near 335 nm.

A search was made for this weak band in the transmission spectra of thin single crystals of RDX and HMX, which are shown in Figures 4a and 4b.

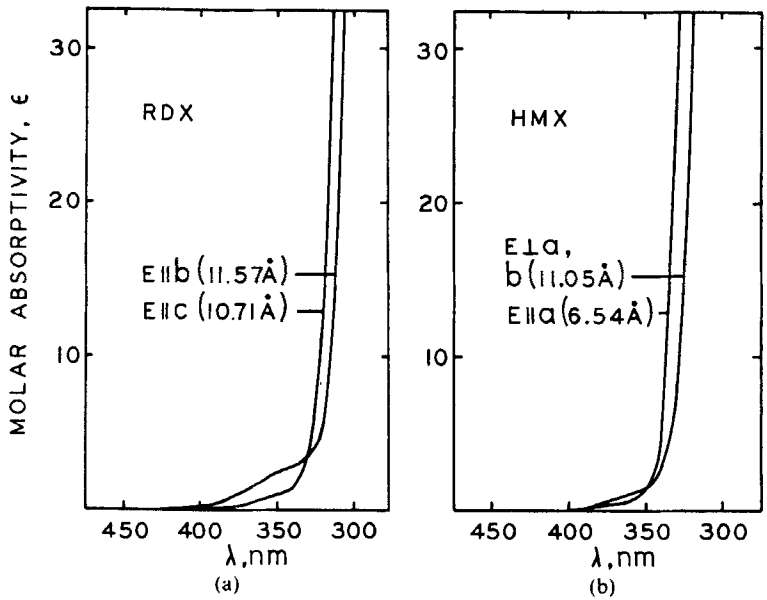

FIGURE 4a (Left) Transmission spectrum of thin (35 micron) RDX single crystal for two mutually perpendicular orientations of polarized light.
4b (Right) Transmission spectrum of thin (1 mm) HMX single crystal for two mutually perpendicular orientations of polarized light.

The absorption is given in terms of the molar absorptivity, ε, in order to facilitate comparison with the solution spectra described below. Weak absorption is seen near 355 nm which may be polarization dependant. Some of the apparent absorption may be due to scattering by crystal surface imperfections. At any rate, the spectra in Figures 4a and 4b can be used to assign an upper limit to the strength of the weak absorption band near 355 nm; this upper bound is $\varepsilon \cong 2$. In addition, it should be noted that the strong absorption of the nitramine band begins near 340 nm in the solid, and that it is polarized parallel to the crystallographic "c" axis of the RDX crystal, and to the "a" axis of the HMX crystal.

The absorption spectra of saturated solutions of RDX and HMX in acetonitrile are shown in Figures 5a and 5b, respectively. It can be seen that at 355 nm the molar absorptivity is 0.04–0.18 L M^{-1} cm^{-1}, some 10–50 times smaller than at the same wavelength in the single crystal spectra of Figures 4a and 4b. There is no discernible peak in this region for solvated RDX or HMX.

No peaks in the region 200–450 nm were detected in the circular dichroism spectra of RDX or HMX in acetonitrile solution.

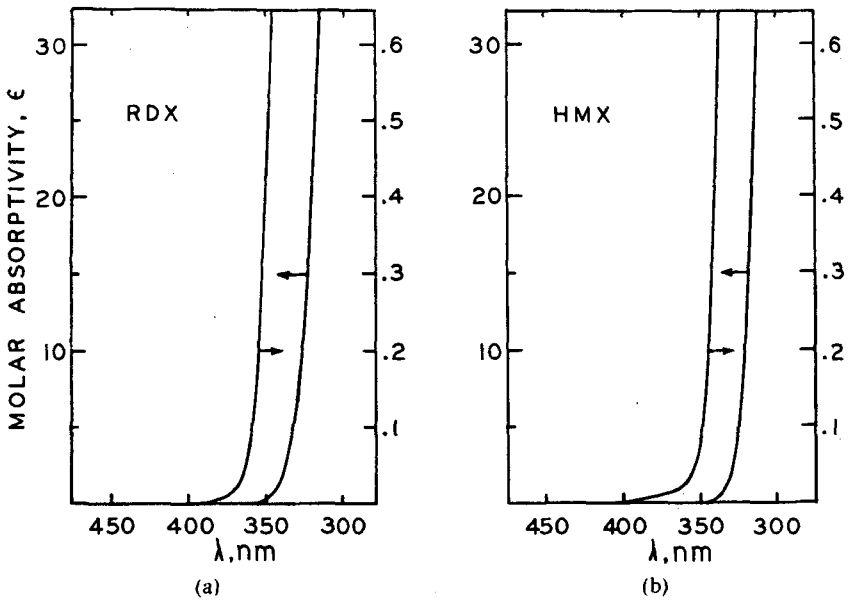

FIGURE 5a (Left) Absorption spectrum of 0.3 M (saturated) solution of RDX in acetonitrile. Path length is 10 cm.
5b (Right) Absorption spectrum of 0.06 M (saturated) solution of HMX in acetonitrile. Path length is 10 cm.

4 DISCUSSION

It is found from the reflectance data that the nitramine band peaks at 255 nm in RDX and at 245 nm in HMX crystals. When compared with the corresponding values[2,3] of 236 nm and 226 nm in acetonitrile solution, it is seen that this band exhibits a substantial red shift upon crystallization. In addition, while the short-wavelength band near 215 nm is the most intense in solvated RDX and HMX, it is the nitramine band which is the most intense in the solid.

The failure to observe the weak band near 355 nm in solution might possibly be caused by a shift to shorter wavelengths upon solvation, and obscuration by the much stronger nitramine band. The technique of circular dichroism is sometimes useful in discerning weak bands hidden under strong ones, as demonstrated by Djerassi, *et al.*, who used it to reveal the presence of a weak band near 350 nm in certain nitro-steroids.[12] Since no band optically active in circular dichroism was uncovered in the spectra of solvated RDX or HMX, this suggests that the weak band observed in specular reflectance is indeed a solid-state effect.

It is interesting to compare the present reflectance results with transmission spectra of films made by evaporation of RDX and HMX solutions published by Maycock, *et al.*[8] The film spectra show absorption in the region 320–400 nm which is much more prominent with respect to the nitramine band than it is in the thin single crystal spectra of Figures 4a and 4b. Such films are expected to have a high density of defects, and it may be that the weak band is associated with the formation of defects. If the band is weak due to some selection rule, absorption might take place primarily at defect sites where the lower site symmetry breaks that selection rule.

Stals[5] has discussed the possibility that the weak band is either the nitramine band, red-shifted by crystallization, or a Davydov component of the nitramine band, red-shifted by resonance interaction. We have seen above that the red-shift of the nitramine band upon crystallization is about 3,100 cm^{-1} in RDX and 3,400 cm^{-1} in HMX. This shift, though substantial, is not large enough to place the band near 355 nm. In addition, Stals did not have access to transmission spectra of thin single crystals, which would have indicated that the band near 355 nm was much weaker than a red-shifted nitramine band would have been.

The hypothesis that the weak band is a Davydov component of the nitramine band is consistent with the fact that both RDX and HMX have several molecules per unit cell, which renders such a splitting possible. In addition, the lower energy component of such a multiplet is often forbidden, which could account for the low intensity of the 355 nm band. However, it

is necessary to account for the 12,000 cm^{-1} red-shift from the position of the nitramine band in the solid. Only in the case of the strongest transitions, such as the 250 nm system in anthracene where $\varepsilon = 40{,}000$ L M^{-1} cm^{-1} does this splitting approach 14,000 cm^{-1}.[13] In the isolated RDX molecule, the nitramine band has a molar absorptivity of 11,000 L M^{-1} cm^{-1}, and Stals[5] has estimated the expected Davydov splitting in RDX as 2,000 cm^{-1}. Thus, it seems unlikely that the weak band can be a Davydov component of the nitramine band.

Charge-transfer dimers are believed to form in concentrated solutions of certain compounds.[14] The formation of these entities leads to a new absorption band at longer wavelengths than the monomer absorption, and to fluorescence excitation corresponding to this band, which occurs at 350 nm. It is possible to imagine an entire crystal bound by charge-transfer forces. In such a crystal, the charge-transfer band of the dimer would be replaced by a band characteristic of the crystal as a whole. Stals[5] has noted that charge-transfer bands normally lie *above* the first singlet exciton band,[15] which according to the calculations of Orloff, *et al.*, would place such a band in RDX at wavelengths shorter than 236 nm. This is indeed true for crystals of the non-polar aromatics, where it is due to the lack of polarization energy to assist in the charge transfer. However, RDX and HMX are highly polar molecules, and it is thus not unreasonable that in these materials a charge-transfer band lie *lower* in energy than the first singlet exciton band, i.e., at wavelengths longer than 236 nm.

Thus it is proposed that the weak 355 nm band in solid RDX and HMX is due to charge-transfer self-complex formation, in agreement with the conclusion of Stals.[5] The band is of low intensity compared to other known charge-transfer bands, perhaps due to some selection rule which renders it forbidden. It is also considered possible that absorption takes place primarily near defect sites where lower local symmetry could break that selection rule.

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