Electronic Absorption Spectra of the 4-R-1,2,4-Triazoline-3,5-diones ($R = H, CH_3, CH_2CH_3, CH_2CH_2CH_2CH_3$)

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Abstract: We report some considerations of the electronic spectroscopy of the 4-R-1,2,4-triazoline-3,5-diones. Vapor and solution spectra were taken and two electronic transitions were found at wavelengths $\geqq 2000$ Å. In the vapor and solution, a weak transition ($f \sim 2 \times 10^{-3}$) is found near 17,600 cm^{-1} and assigned to an azo-centered $n \rightarrow \pi^*$, $^1B_1 \leftarrow {}^1A_1$ transition. In solution, a stronger transition ($f > 6 \times 10^{-2}$) is found at $\sim$35,000 cm^{-1} and assigned to a $\pi \rightarrow \pi^*$, $^1B_2 \leftarrow {}^1A_1$ transition. A simple MO picture of the electronic states is presented as well as a partial analysis of the vibrational structure of the $^1B_1 \leftarrow {}^1A_1$ transition for 4-methyl-1,2,4-triazoline-3,5-dione. Comments are made concerning the relationship of this work to some of the photochemistry of these compounds.

The chemical properties of the class of compounds, the 4-R-1,2,4-triazoline-3,5-diones, have been extensively studied because of their extremely high reactivity as a dienophile in a Diels–Alder reaction.[2–6] However, little spectroscopic information is available except for that reported by Stickler,[7] Stickler and Pirkle,[8] and Cookson, *et al.*,[4] these being done for identification purposes. Spectroscopic information concerning these compounds is of importance for a number of reasons. First, these compounds exhibit rather unique photophysical properties; spectroscopic information is necessary for interpretations of these properties. Next, Stickler has shown that besides the Diels–Alder reactivity, these compounds react photochemically with compounds having easily abstractable protons and with themselves to form polymers. Hence, spectroscopic work may shed some light on the photochemical processes. Further, these compounds are iso-π-electronic with the compounds *N*-R-maleimide and maleic anhydride recently studied by Seliskar and McGlynn[9,10] and may provide some interesting comparisons. In the same vein, the compounds studied by Seliskar and McGlynn as well as the triazoline diones are electronically and structurally similar to a large number of biochemically interesting molecules. The five-membered heterocyclic ring structure is very often found to be a component in large porphorin type compounds. Finally, these compounds present a somewhat unique situation in that they contain the two best known n,π^* chromophores (>C=O and -N=N-) in close proximity connected through a conjugated system, hence providing interesting subjects for theoretical calculations.

Experimental Section

Synthesis. The 4-R-1,2,4-triazoline-3,5-diones (hereafter designated "R-TAD") were synthesized using the method of Stickler and Pirkle.[8] However, solid R-urazole was oxidized by passing $N_2O_4(g)$ directly over it, eliminating the necessity of evaporating any solvent. In this same way, enough of the extremely unstable H-TAD was synthesized to procure a solution spectrum. All of the samples were sublimed at least once under high vacuum.

Vapor-Phase Absorption Spectra. The vapor-phase absorption spectra were recorded photoelectrically using a Spex 1700-III, 3/4 m Czerny-Turner scanning spectrometer fitted with a 1200 l./mm grating blazed at 5000 Å. The excitation source was a Hanovia 150-W high-pressure Xe arc lamp. The absorption cell was a Pyrex tube, 1.25 m long wrapped in heating tape and glass wool insulation. The temperature of the cell was monitored by five Fenwal Electronics thermistors and was varied between 60 and 100° depending on the R-TAD studied.

For methyl-TAD, the absorption spectrum was calibrated with an Fe/Ne hollow cathode lamp by interposing the methyl-TAD absorption bands between portions of lamp emissions. A dispersion curve was calculated using a least-squares fit and the wavelengths of methyl TAD absorptions were obtained from this dispersion curve. Since the spectra for the other R-TAD's were not nearly as structured as the methyl-TAD spectrum, calibrated markers from the Spex were used to obtain the wavelengths.

Solution and Ir Spectra. The solution spectra were measured using a Cary 14 spectrometer. The solvents were spectral grade and dried over an appropriate drying agent, since R-TAD appears to be highly moisture sensitive. An ir spectrum of methyl-TAD was also taken using CsBr plates, a Nujol mull, and a Beckman IR-20 spectrometer.

General Features of the Spectra. Vapor-Phase Spectra. Vapor-phase spectra were recorded for the electronic transition which extends from $\sim$17,600 to $\sim$20,200 cm^{-1} in methyl-, ethyl-, and *n*-butyl-TAD. These spectra are shown in Figure 1. In all cases, vibronic structure is distinctly observable with four fairly intense absorptions (at $\sim$17,600, $\sim$18,200, $\sim$18,560, and $\sim$19,160 cm^{-1}) dominating the spectra. A weak absorption ($\sim$17,940 cm^{-1}) is noted between the first two intense absorptions. Methyl-TAD displays considerable structure associated with each vibronic band, the extent of the structure being somewhat temperature dependent. To the longer wavelength side of $\sim$17,600 cm^{-1} absorptions are a number of weak bands with temperature dependent intensities.

Solution Spectra. In Figure 2 are shown spectra of methyl-, ethyl-, and *n*-butyl-TAD taken in *n*-hexane and the spectrum of H-TAD taken in CCl_4. For each of the alkyl-TAD's, the vibrational structure is very similar to the gas-phase spectra and they are very similar to each other. H-TAD displays a slightly different vibrational structure in that the two intense peaks in the alkyl TAD's at $\sim$18,000 and 18,400 cm^{-1} disappear and are replaced by one centered at $\sim$18,200 cm^{-1}. Further, it is noted that the wavelength of the longest wavelength principal absorption is essentially constant for all of the N substituents including R = H. Also, another absorption at $\sim$19,000 cm^{-1} is fairly constant. Oscillator

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[1] (a) Mobil Oil Foundation Fellow, 1971–1972; (b) Alfred P. Sloan Fellow, 1972–1973.

[2] S. S. H. Gilani and D. J. Triggle, *J. Org. Chem.*, **31**, 2397 (1966).

[3] J. Sauer and B. Schroder, *Chem. Ber.*, **100**, 678 (1967).

[4] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1904 (1967).

[5] (a) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Lett.*, 615 (1962); (b) M. G. de Amezua, M. Lora-Tamayo, and J. L. Soto, *ibid.*, 2407 (1970).

[6] B. T. Gilis and J. T. Hagarty, *J. Org. Chem.*, **32**, 330 (1967).

[7] J. C. Stickler, Ph.D. Thesis, University of Illinois, 1971.

[8] J. C. Stickler and W. H. Pirkle, *J. Org. Chem.*, **31**, 3444 (1966).

[9] C. J. Seliskar and S. P. McGlynn, *J. Chem. Phys.*, **55**, 4337 (1971).

[10] C. J. Seliskar and S. P. McGlynn, *ibid.*, **56**, 275 (1972).

Table I. Spectral Data for R-TAD's in CCl_4 Solution

Compd	Transition	λ_{max}, Å	$\bar{\nu}_{max}$, cm^{-1}	ϵ_{max}, l./cm mol	f
H-TAD	$n \rightarrow \pi^*$	5483	18,233		
Methyl-TAD	$n \rightarrow \pi^*$	5417	18,455	249	$2.03 (\pm 0.2) \times 10^{-3}$
Ethyl-TAD	$n \rightarrow \pi^*$	5436	18,391	230	$2.05 (\pm 0.2) \times 10^{-3}$
n-Butyl-TAD	$n \rightarrow \pi^*$	5437	18,387	242	$2.22 (\pm 0.2) \times 10^{-3}$
Methyl-TAD	$\pi \rightarrow \pi^*$	2885	34,652	1717	(0.06)[a]
Ethyl-TAD	$\pi \rightarrow \pi^*$	2867	34,869	2115	(0.07)[a]
n-Butyl-TAD	$\pi \rightarrow \pi^*$	2958	33,797	1737	(0.06)[a]
H-TAD	$\pi \rightarrow \pi^*$	2728	36,646		

[a] Represents a *lower bound* for the oscillator strength.

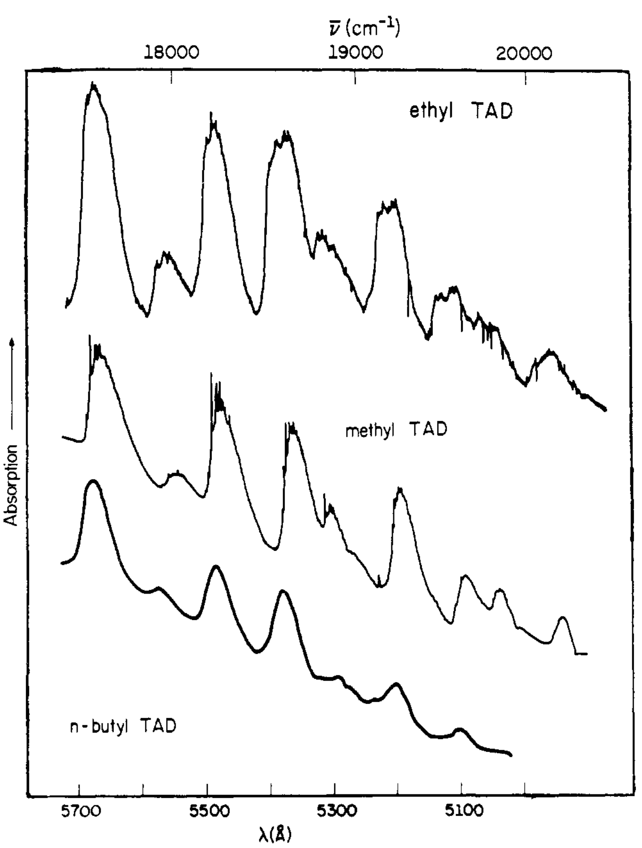

Figure 1. Moderate resolution vapor-phase absorption spectra of the lowest energy singlet transition in the 4-R-1,2,4-triazoline-3,5-diones, R = CH_3, CH_2CH_3, $CH_2CH_2CH_2CH_3$. Absorption is to the top of the figure.

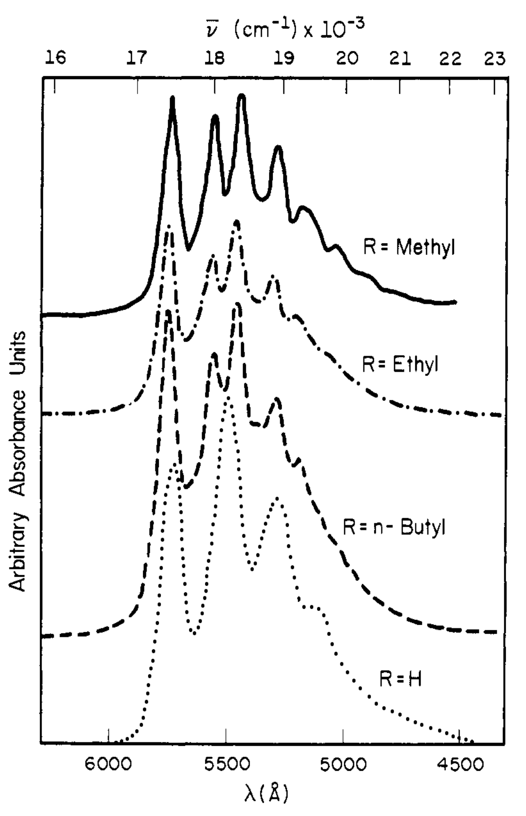

Figure 2. Solution absorption spectra of the lowest energy singlet in the 4-R-1,2,4-triazoline-3,5-diones; R = alkyl are in *n*-hexane; R = H is in CCl_4. Arbitrary absorbance units.

strengths determined for each of the alkyl-TAD's are listed in Table I. Also listed are the λ_{max} and ϵ_{max}. The oscillator strengths of the different alkyl-TAD's are identical within experimental accuracy. Solvent shifts of the absorption maxima were found to be hypsochromic (*i.e.*, to shorter wavelengths) in a series of solvents of increasing dielectric constant (CCl_4, CH_2Cl_2, and CH_3CN). This hypsochromic shift is accompanied by blurring of the vibronic structure. In CH_3CN, the vibronic structure is indiscernible.

In solution, a higher energy transition was also investigated. This transition has an intensity maximum at ~35,000 cm^{-1} for the alkyl-TAD's and at ~36,600 cm^{-1} for H-TAD and is more intense than the transition discussed above. A *lower bound* for the oscillator strength of this transition is listed in Table I for each of the alkyl-TAD's. Solvent shift information was difficult to obtain due to the lack of discernible features in the spectrum. Qualitatively, though, the shift is either zero or bathochromic (*i.e.*, to longer wavelengths).

Discussion

Molecular Orbitals. Although the geometry for R-TAD is not known with certainty, it seems likely that the ring is planar or near planar with a structure similar to that shown in Figure 3. The similarity of the spectra for different R groups suggests that the molecular states can be adequately described by considering only the MO's on the TAD ring, for which the point group is C_{2v}. The axes are designated according to the recommendations of the Lund Meeting,[11] *i.e.*, x axis perpendicular to the TAD ring.[12] The atomic p_π and heteroatom n orbitals are shown and designated in Figure 3. The out-of-plane p_π orbitals are indicated by open circles containing designations for the certain atom and the black dots denote in-plane nonbonding nitrogen sp^2 orbitals and oxygen p_n orbitals. Using the usual symmetry methods,[13] the proper symmetry

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(11) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1997 (1955).

(12) We must note that this designation of axes is different from that of Seliskar and McGlynn,[9,10] since they defined the y axis to be perpendicular to the molecular plane.

(13) Examples of these methods can be found in many books on group theory; *e.g.*, see D. S. Schonland, "Molecular Symmetry," D. Van Nostrand, London, 1965, pp 181–211; F. A. Cotton, "Chemical Applications of Group Theory," Interscience, New York, N. Y., 1963, pp 117–155; M. Orchin and H. H. Jaffé, "Symmetry, Orbitals, and Spectra," Wiley-Interscience, New York, N. Y., 1971, pp 263–294.

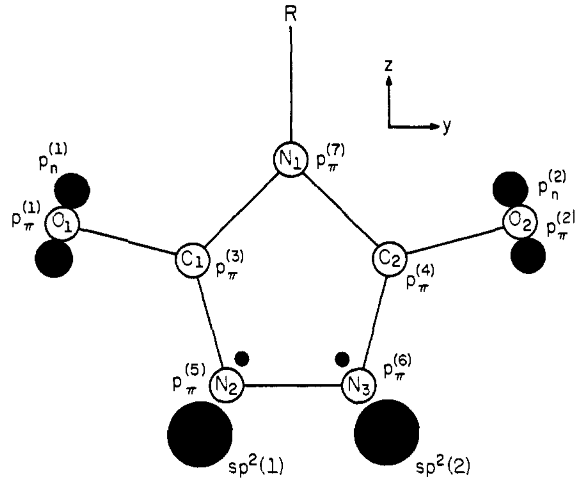

Figure 3. Schematic representation of the R-TAD molecular structure and the AO's needed for an LCAO-MO description of the electronic states. The open circles are out-of-plane p_π orbitals; these circles also contain a designation for the atom. The black dots are in-plane nonbonding orbitals. The axis designation is shown with the x axis being out of plane.

combinations of the p_π and nonbonding orbitals can be made. A Hückel MO calculation, for which the values of the Coulomb and resonance integrals were obtained from Suzuki,[14] was performed in order to obtain the relative energy ordering of the π LCAO-MO's. The qualitative ordering of the nonbonding MO's is obtained by noting that nitrogen valence AO Coulomb integrals are usually less negative than those for oxygen valence AO's and by noting that for a cis-azo configuration the asymmetric combination of AO's is higher in energy than the symmetric combination.[15,16] A pictorial representation of these qualitative considerations and of the results of the Hückel calculation is shown in Figure 4. A designation for each MO and its symmetry is shown on the right-hand portion of the figure. The filled and unfilled circles in the figures represent plus and minus lobes of the AO's, respectively. For the *n* MO's (+) denotes a symmetric combination and (−) an asymmetric combination.

Electronic State Designations. Because of the characteristics of the low-energy transition described above and in Table I, we believe it to be n → π^* in nature. Further, since $f \simeq 2 \times 10^{-3}$ and $\epsilon_{max} \simeq 240$, we believe it is local symmetry allowed, unlike usual carbonyl n → π^* transitions.[17,18] Therefore, we may conclude that the absorption arises primarily from the promotion of an electron from $n^{(2)}(-)$ to π_5, forming a $^1B_1$ n,π^* state. In a similar manner, because of the characteristics of the higher energy transition, we may conclude that it originates from the promotion of an electron from π_4 to π_5 forming a $^1B_2$ π,π^* state.

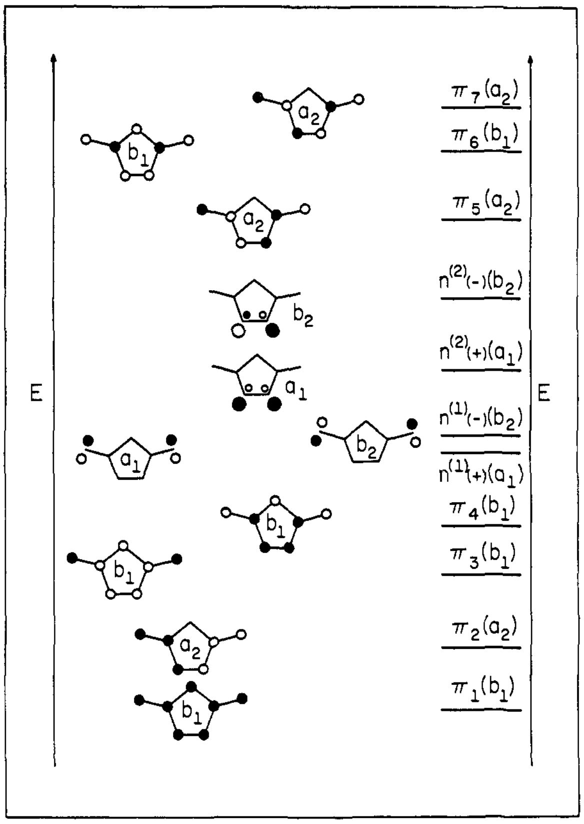

Figure 4. Schematic representation of the R-TAD molecular orbitals. The right-hand side of the figure shows the relative energy ordering of the various MO's (see text) and a designation for each. The stick figures indicate the MO's, with black and white dots being + and − lobes of the AO's, respectively. The MO's designated as π_i are out-of-plane while the MO's designated as n are in-plane. Also given are the various symmetries of the MO's.

The above considerations are consistent with a number of other qualitative observations. First, the assumption of a C_{2v} point group for the description of the molecular states tacitly assumes that the R group has little or no effect upon the electronic structure of the ring. This assumption is supported by the solution spectrum of phenyl-TAD reported by Cookson, *et al.*,[4] which exhibits absorptions similar to both TAD ring and benzene absorptions. Second, the $^1B_1 \leftarrow {}^1A_1$ transition should be relatively insensitive to the nature of the R group since N_1, to which R is attached, is not involved in the n or π MO's which make up $^1B_1$. The $^1B_2 \leftarrow {}^1A_1$ transition, however, should be affected by the nature of the substituent (as observed, see Table I) since π_4 of $^1B_2$ contains $p_\pi^{(7)}$ while π_5 does not. The 1600-cm^{-1} shift upon methylation of H-TAD is in the proper direction according to simple composite molecule considerations.[19] Third, it is observed that the oscillator strength for $^1B_2 \leftarrow {}^1A_1$ is considerably lower than that expected for a fully allowed $\pi \rightarrow \pi^*$ transition.[20] This can also be understood because it is a transition from a state having nodes between atoms to a state having a node on an atom; hence there may be overlap forbiddeness.

Vibrational Assignments. We have carried out a partial vibrational analysis of the lower energy transition in vapor-phase methyl-TAD (see Figure 1). Since $^1B_1 \leftarrow {}^1A_1$ is x dipole allowed, the 0-0 band should be prominent. The intensity of the band at ~17,600 cm^{-1} and its position with respect to the vibrational

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(14) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, Chapter 9.

(15) Reference 14, p 500.

(16) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, 17, 1248 (1949).

(17) J. W. Sidman, *Chem. Rev.*, **58**, 691 (1958).

(18) Reference 14, pp 75–78, 221.

(19) Reference 14, pp 408–410.

(20) Reference 17, p 709.

Table II. Equations Describing Position of Absorbances in Vapor Spectrum of Methyl-TAD

Equation $\bar{\nu}_{0-0} = 17{,}607.5$	Region of applicability, cm^{-1}	$\lvert\bar{\nu}_{\text{calcd}} - \bar{\nu}_{\text{obsd}}\rvert_{\text{av.}}$ cm^{-1}
$\bar{\nu} = \bar{\nu}_{0-0} + l366.8 + m586.1 + n966.9 + p1549.7 - q11.5$ $[0 \leq l \leq 1, 0 \leq m \leq 3, 0 \leq n \leq 2, 0 \leq p \leq 1,$ $0 \leq q \leq 2]$	17,584–19,970 (main progression)	±2.4
$\bar{\nu} = \bar{\nu}_{0-0} + l18.5 + m21.5 + n25.2 - p11.5 - q82.7 -$ $r176.5 - s383.8 - t626.7$ $0 \leq l \leq 2, 0 \leq m \leq 3, 0 \leq n \leq 2, 0 \leq p \leq 2, 0 \leq q \leq 1,$ $0 \leq r \leq 1, 0 \leq s \leq 1, 0 \leq t \leq 1$	16,983–17,607 (hot bands)	±2.0
$\bar{\nu} = \bar{\nu}_{0-0} + l18.5 + m21.5 + n25.2 - p11.5$ $[0 \leq l \leq 5, 0 \leq m \leq 5, 0 \leq n \leq 7, 0 \leq p \leq 2]$	17,584–17,773 (0–0 band)	±0.8
$\bar{\nu} = \bar{\nu}_{0-0} + 586.1 + l20.6 + m22.9 + n27.1 - p11.5$ $[0 \leq l \leq 5, 0 \leq m \leq 4, 0 \leq n \leq 5, 0 \leq p \leq 2]$	18,166–18,326 (586-cm^{-1} band)	±0.9

Table III. Tentative Assignment of Observed Vibrational Frequencies and Comparison of Normal Coordinate Analysis

Symmetry		Calcd, cm^{-1}	Obsd ground, cm^{-1}	Obsd excited, cm^{-1}	Description
C_s	C_{2v}				
a′′	b$_1$	410	382^a 382^c	366^b	Carbonyl out of plane wag, N$_1$–CH$_3$ out of plane deformation
a′	a$_1$	690	625^a 625^c	586^b	Carbonyl in plane wag, N$_1$–CH$_3$ stretch
a′	a$_1$	1200	1278^a	966^b	Carbonyl in plane wag, N$_1$–CH$_3$ stretch, azo outward stretch
a′	a$_1$	1560	1530^a	1549^b	Azo outward stretch, carbonyl stretch

^{a} Observed in infrared spectrum. ^{b} Observed in progressions in electronic absorption spectrum. ^{c} Observed as hot bands in electronic absorption spectrum.

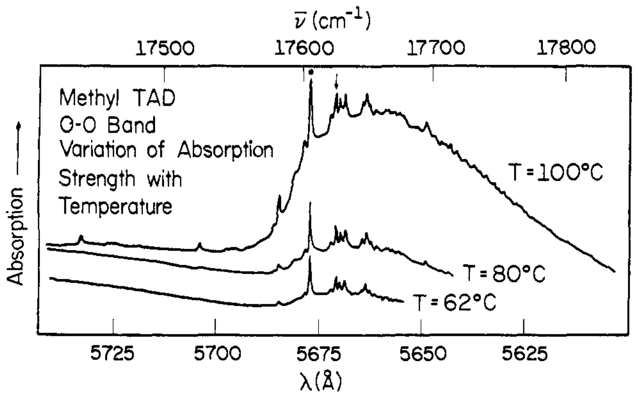

Figure 5. Expanded spectrum of the 0–0 band in methyl-TAD showing the vibronic structure. The star (*) indicates our assigned 0–0 absorption, while the arrow indicates the peak used to calculate intensity ratios to investigate the temperature dependence.

spacings and hot bands lead us to assign it as the 0–0 band. The temperature dependence of the 0–0 band is shown in Figure 5. Although the concentration of methyl-TAD varied with temperature of the cell, we believe the peak at 17,607 cm^{-1} (indicated by the star) shows substantially less temperature dependence (see below) than the associated absorbances. We have chosen this absorption at 17,607 cm^{-1} as the origin of the $^1B_1 \leftarrow {}^1A_1$ transition. In the same manner, we have chosen the most prominent, lowest energy feature in each vibronic band as the origin of each band.

Energy differences from the 0–0 absorption were measured. We found that we could fit the principal absorptions in several regions by the fairly simple equations listed in Table II. The regions of applicability of these equations are also listed as well as the average deviations of the fits. The observed structure in the higher energy bands could not be fit to such simple equations.

A normal coordinate analysis was attempted using a program described by Gwinn.[21] This analysis is necessarily approximate since the bond parameters and force constants are not known for the TAD's. Nevertheless, bond lengths, angles, and force constants for methyl-TAD were obtained from analogous compounds.[22–24] The results of these calculations are compared with observed ground state and excited-state energies in Table III. The symmetries of the vibrations under C_{2v} and C_s are also listed as well as a description of the vibrations. We note that all of the vibrations except one are allowed by the b$_1$, x dipole. Further calculations were carried out on H-TAD and we were able to reproduce the "replacement" of the 586- and 966-cm^{-1} (methyl-TAD) vibrations by one at ~870 cm^{-1} (H-TAD) (see Figure 2). We also were able to reproduce the constancy of the 1560-cm^{-1} vibration between H-TAD and methyl-TAD (see Figure 2). Our normal coordinate analysis, then, seems at least qualitatively consistent with experiment.

As mentioned previously, each band contains a fair amount of blue-shaded vibronic structure. Two pos-

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(21) W. D. Gwinn, *J. Chem. Phys.*, **55**, 477 (1971).

(22) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

(23) "Tables of Interatomic Distances and Configurations in Molecules and Ions," *Chem. Soc., Spec. Publ.*, **No. 18** (1965).

(24) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand-Reinhold, New York, N. Y., 1945, pp 193, 195.

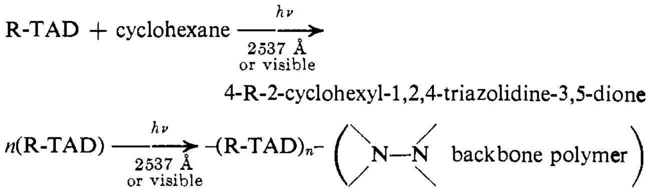
sible explanations are (1) sequence bands from ground-state vibrations having energies lower than the corresponding excited state vibrations or (2) three low-lying excited-state vibrations of ~20 cm^{-1}. Although the normal coordinate analysis does give such vibrations (primarily methyl group distortions), the variation of absorption strength with temperature is indicative of sequence bands. This is shown by the following ratios of line heights comparing the 17,607-cm^{-1} absorption (star in Figure 5) to the absorption at 17,626 cm^{-1} (arrow in Figure 5): 1.07 at 100°, 1.48 at 80°, and 1.64 at 62°. This though is not a complete test since an integrated intensity might show different ratios.

Relations to Other Work. In the work done by Seliskar and McGlynn, it was found that a bathochromic shift took place in going from maleimide to *N*-methylmaleimide in the $^1B_2 \leftarrow {}^1A_1$ (their $^1B_1 \leftarrow {}^1A_1$) transition.[12] Since the π system of these molecules and the TAD's should be similar, our results, showing a bathochromic shift in $^1B_2 \leftarrow {}^1A_1$ in going from H-TAD to methyl-TAD and our simple MO scheme, are consistent with their results. We have also performed π-electron density calculations using the usual formula[25] and the results are shown in Table IV. As can be seen, the π,π^* state shows a decrease in the electron density at N_1 in comparison to the ground state. This calculation is consistent with Seliskar and McGlynn's hypothesis tht N_1 should act as an "electron donor" in $^1B_2 \leftarrow {}^1A_1$ in maleimide.[26] We have, however, found no evidence of another $n \rightarrow \pi^*$ transition which would correspond to the one observed by Seliskar and McGlynn.[9] This would be a $n^{(1)}(-) \rightarrow \pi^*$; $^1B_1 \leftarrow {}^1A_1$ (their $^1B_2 \leftarrow {}^1A_1$). Seliskar and McGlynn found this transition to be very weak and almost coincident with the lowest $\pi \rightarrow \pi^*$ transition. Our MO considerations indicate that this transition may very well be coincident with our $^1B_2 \leftarrow {}^1A_1$ or even higher in energy.

Table IV. Partial π-Electron Densities for the Electronic States of the 4-R-1,2,4-Triazoline-3,5-diones

Atom	State $^1A_1$	 $^1B_1$	 $^1B_2$
N_1	1.738	1.738	1.543
N_2, N_3	0.938	1.175	0.786
C_1, C_2	0.452	0.640	0.639
O_1, O_2	1.724	1.797	1.786

We would also like to indicate that the simple MO considerations presented here may help to understand the photochemical reactions observed by Stickler.[27]



$$\text{R-TAD} + \text{cyclohexane} \xrightarrow[\text{2537 Å or visible}]{h\nu} \text{4-R-2-cyclohexyl-1,2,4-triazolidine-3,5-dione}$$

$$n(\text{R-TAD}) \xrightarrow[\text{2537 Å or visible}]{h\nu} \text{-(R-TAD)}_n\text{-} \quad (\text{N—N backbone polymer})$$

According to the MO scheme, excitation to the $^1B_1$ state causes a decrease in the n electron character at the azo nitrogens, hence producing a species resembling a free radical which is a likely intermediate in an abstraction or polymerization reaction. Indeed Stickler[28] has observed an esr spectrum in a photochemical reaction mixture which is indicative of a free radical intermediate. It is also interesting to note that excitation to $^1B_2$ gives the same photoproduct. Rapid internal conversion between $^1B_2$ and $^1B_1$ could explain this and indeed excitation to $^1B_2$ results in strong visible fluorescence from $^1B_1$.[29]

Summary

The visible and ultraviolet regions of the absorption spectra of the R-TAD's show two absorptions. Assignment to the weaker transition at 17,600 cm^{-1} is made to be $^1B_1 \leftarrow {}^1A_1$ and the stronger at ~35,000 cm^{-1} is made to be $^1B_2 \leftarrow {}^1A_1$. The assignment was made by solvent shifts, *f* numbers and a simple Hückel LCAO-MO calculation. Analysis of the vibrational structure of the $^1B_1 \leftarrow {}^1A_1$ transition in methyl-TAD was attempted and found to contain four fundamentals of 366 cm^{-1} (b_1), 586 cm^{-1} (a_1), 966 cm^{-1} (a_1), 1549 cm^{-1} (a_1). Conjecture was made concerning an explanation of the source of the blue-shaded band structure. The MO theory was used to explain some of the photochemistry.

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(25) M. Orchin and H. H. Jaffé, ref 13, p 277.

(26) C. J. Seliskar and S. P. McGlynn, *J. Chem. Phys.*, **56**, 1417 (1972).

(27) Reference 8, pp 24–55.

(28) Reference 8, p 48.

(29) W. H. Pirkle, private communication.