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Radiationless Decay in the Azabenzenes as Studied by Opto-Acoustic Spectroscopy

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Received September 5, 1974

Abstract: In the broadest terms, two classes of relaxation behavior are observed in the azabenzenes. (i) In pyridine, pyridazine, *sym*-tetrazine, and probably *sym*-triazine, the relaxation rates to the ground state following $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations are equally fast on our time scale ($k \geq 10^6$ sec^{-1}). In the presence of biacetyl, the relaxations from the $^1(n,\pi^*)$ states of pyridine and *sym*-triazine are noticeably slowed, but not those in *sym*-tetrazine or pyridazine. Relaxation from the $^1(\pi,\pi^*)$ states are not affected by the addition of biacetyl. (ii) In pyrazine, pyrimidine, and 2,6-dimethylpyrazine, the $^1(n,\pi^*)$ relaxation rate is significantly slower than that from $^1(\pi,\pi^*)$ and becomes even slower in the presence of biacetyl. However, in the presence of oxygen, the two rates are both very fast, except in the case of 2,6-dimethylpyrazine. Tetramethylpyrazine probably belongs in this second class. It is clear in the optical spectra of the diazines that a new relaxation channel opens up within the S_1 band envelope; this new channel is tentatively identified as $S_1 \rightarrow T_3$ relaxation. In all cases, it appears that the $S_2(\pi,\pi^*)$ state relaxes rapidly and avoids the S_1, T_2, T_1 levels on its way to the ground state. There is some evidence that symmetry-determined spin–orbit matrix elements are important in determining the rates of $^1(n,\pi^*)$ relaxation in certain of these compounds.

The azabenzenes, from pyridine to tetrazine, have been the objects of spectroscopic and photochemical studies for many years, and deservedly so.[1,2] Paralleling this experimental work on the excited states are several dozens of theoretical calculations on spectral excitation energies, intensities, etc., in these systems. Clearly, the azabenzenes have become a cornerstone of molecular spectroscopic research. As in almost all polyatomic molecules, that area of azabenzene spectroscopy still in great need of study involves the paths by which these excited molecules relax, in particular, the paths for radiationless relaxation. To this end, we have performed a low-resolution study of the azabenzenes and some of their derivatives in the 7000–2200 Å region using the relatively new technique of opto-acoustic spectroscopy.

Following the act of absorption, that fraction of the molecules electing radiationless decay cascade down the myriad electronic–vibrational–rotational ladders to the ground state thereby releasing heat. By opto-acoustic spectroscopy, one is able to measure the relative amounts of heat released and the relative temporal relationships between heats released at different points in the spectrum but, since there is no a priori way of relating these observations to any specific step in the relaxation chain, such data by itself is difficult to interpret unambiguously. Hence, we strive to correlate our work with other, more conventional experiments.

In the opto-acoustic experiment, pulses of monochromatic light are passed into a gas cell and, if these are absorbed and thence degraded to heat, i.e., kinetic energy of the surrounding gas, a pressure wave is generated which can be sensed by a microphone. Using phase-sensitive detection and a monochromator, the spectrum of the incident light can be scanned giving the relative amount of heat and a phase angle related to the overall relaxation rate at each wavelength.[3-5] Of course, the amount of heat generated at each wavelength will depend upon the light intensity incident at that wavelength; this factor has not been allowed for in the present spectra and results in seemingly anomalous intensity ratios. (See Figure 2 of ref 3 for the power spectrum of the lamp.)

The phase-angle measurement is especially interesting because its abrupt changes of slope often show the presence of relaxation channels opening up at specific points in the opto-acoustic spectrum, which are otherwise missing in the absorption spectrum. These new channels could represent relaxation via higher singlet states, via higher triplet states as suggested bv Loar et al.[6] in the case of anthracene, or relaxation via photodecomposition and recombination.

With a gas of a given composition and pressure in the cell, all of the available information which one can obtain in this way is contained in a heat-amplitude scan and a phase-angle scan. Such data in the 7000–2200 Å range is presented here. While the heat-amplitude scans at two fixed phase angles separated by 90° are run automatically, the phase-angle scans were determined manually by measuring the phase angle for a null signal at each wavelength, while chopping at 100–1000 Hz. At these frequencies, one can discriminate between two relaxations differing by about 10^{-6} sec or more, that is to say, any two processes both going faster than about 10^6 sec^{-1} will have the same phase angle in this experiment, no matter how large the difference. Changes of phase angle with wavelength in these experiments imply mean lifetimes of 10^{-2} to 10^{-6} sec for radiationless relaxation.

It is helpful to think of the heat signal in the opto-acoustic experiment as a polar vector, where the vector magnitude is proportional to the magnitude of the heat released, and its angle is related to the time lag for its release. In the case of overlapping bands, or of simultaneous decay via separate channels, the heat released will be characterized by several such vectors, but the signal measured will correspond to the vector sum and may be positive in some spectral regions and negative in others. In the case of a cascade, the tangent of the overall phase angle is the sum of the tangents of the component one-step phase angles.

At any one wavelength, the phase angle as measured is a sum of the instrumental time lag θ_I and the time lag inherent in the overall radiationless relaxation θ_R. If the fastest relaxation in a molecule is taken as faster than 10^6 sec^{-1}, i.e., infinite, then its phase angle provides a reference point in the sense that it can be taken as the instrumental lag. One then applies eq 1 in order to estimate the lifetime (τ_R)

$$\tan(\theta_R - \theta_I) = 2\pi\omega\tau_R \qquad (1)$$

of the nonradiating state, assuming that it decays exponentially in a pseudo-unimolecular process;[7] ω is the chopping frequency. Of course, the upper limit to the measurable speed can be increased somewhat by chopping at higher frequencies, but the temporal resolution attainable is still limited by the high-frequency response of the microphone (ca. 10^6 Hz).

If vibrational relaxations in the large molecules studied here were all very fast (at essentially the collision rate), then the observed changes of phase angle would correspond to changes of the electronic states involved in the relaxation, and the phase-angle spectrum would be a step spectrum. On the other hand, we observe much more gradual changes of phase angle which may result from several different causes. In order of likelihood they are the following. (i) Spectral overlap of two absorption bands relaxing at different rates will result in a gradual change of phase angle as one scans from one band to the other. (ii) The total heat vector includes a fast vibrational relaxation component, the magnitude of which increases with increasing vibrational excitation. (iii) The Franck–Condon factors may vary strongly throughout a band, thus influencing the rates of interstate tunneling.[8] (iv) A changing density of states will affect the rate of interstate tunneling. (v) There may be a gradual change of electronic-state character due to spin–orbit or vibronic mixing throughout a band so that the intersystem crossing probabilities vary with vibrational quantum number. (vi) The rates of vibrational relaxation may be slow and vary with vibrational quantum number.

Finally, it must be pointed out that crossings from one surface to another may lead to dissociation and, though rapid, the products (radicals) may thereafter react far more slowly to release heat. The overall effect on the phase angle, then, is to increase it greatly. This is apparently not an important factor when working with the azabenzenes, for the quantum yields for photochemistry are very small.[9]

In the case of intersystem crossing, which plays a very important role in azabenzene relaxation, it is generally acknowledged that a prime factor in determining the relaxation rate is the spin–orbit matrix element between the relevant singlet and triplet states. Qualitatively, the rate of intersystem crossing is ca. 10^3 larger when the states (n,π^*) and (π,π^*) are connected by a nonzero spin–orbit matrix element, than when the states are both (n,π^*) or both (π,π^*).[10] Because this generalization too is subject to the vagaries of Franck–Condon factors and densities of states which may act to slow an otherwise rapid surface crossing, its utility is questionable in theory but, practically, it often describes the real situation. Though we use this as a simple guide, Azumi has suggested that in compounds of this type, the situation may be far more complex.[11]

In several cases, interesting kinetic effects result from adding a second gas,[4] which may alter the flow of heat either through collisional deactivation, energy transfer, complex formation, or photochemical reaction. The addition of biacetyl is very interesting in this respect, and we have made it a routine part of our program to observe the effects on the opto-acoustic spectrum of adding this substance. In addition to biacetyl, the effects of adding nitrogen, oxygen, and *cis*-butene-2 are also reported. The azabenzenes were purified either by gas chromatography or sublimation, and the added gases were of the highest purity available commercially.

Biacetyl

Since biacetyl is a prominent component of our studies on the azabenzenes, it is useful to present a few of its opto-acoustic properties, for later reference.[5] Everything we need to know is contained in Figure 1. The in-phase and out-of-phase opto-acoustic spectra show that S_2 and the short-wavelength part of S_1 seem to relax at approximately the same rate, whereas the phase angle which nulls S_2 leaves the long-wavelength part of S_1 unchanged. The relationship is clearer if one instead considers the phase angle which nulls the spectrum at each wavelength (Figure 1). We measure a constant phase angle from 4600 to 4430 Å indicating a constant rate of relaxation as the various vibronic relaxations pass through a common bottleneck. This phase angle corresponds to the rapid $S_1 \rightarrow T_1$ intersystem crossing, followed by the spin-orbit forbidden $T_1 \rightarrow S_0$ intersystem crossing. At 4430 Å, there is a sharp break in the phase as the rate of relaxation accelerates. This marks the threshold for relaxation via the T_2 state, and the rate then increases from this point.

As one excites higher into S_1, there accumulates a larger excess of vibrational energy which is quickly relaxed upon collision. From this source, there results a fast component to the overall heat which becomes larger as the wavelength decreases and should act to lower the phase angle, in agreement with the observation. However, were this the cause of the decreasing phase angle in the S_1 band (Figure 1), then the quantum yield for phosphorescence from the $v = 0$ level of T_1 would remain independent of exciting wavelength. In fact, the quantum yield decreases rapidly as the wavelength decreases[12] showing that the fast relaxation does not populate T_1, but instead competes with relaxation to that state with increasing efficiency as one goes up the vibrational ladder. This is consistent with S_1 deexcitation via T_2 becoming more and more prominent as the wavelength decreases in S_1. Such a situation could arise if the vibrational overlap between S_1 and T_2 sublevels were becoming far larger than those between S_1 and T_1, or if the rate were dependent upon the density of levels in T_2.

At the S_2 threshold (3300 Å), the phase angle reaches its instrument-limited value and levels off. It is this remarkably large phase-angle difference of 45° (at 400 Hz) between S_2 and the front of S_1 in biacetyl which makes energy transfer to S_1 or T_1 of biacetyl from an otherwise rapidly relaxing system so obvious in the out-of-phase spectrum. Using eq 1 and the assumption that S_2 is relaxing infinitely fast, the long-wavelength part of S_1 is relaxing at an overall rate of 2.5×10^3 sec^{-1}.

As discussed above, it has been our view that the slow heat coming from a second molecule in the presence of biacetyl resulted from energy transfer to T_1 of biacetyl and slow $T_1 \rightarrow S_0$ relaxation from there. Emeis et al.,[13] however, show that the slow-heat effect of biacetyl in acetaldehyde does not have the same spectral form as does the sensitized T_1 phosphorescence excitation spectrum, and that energy transfer to produce highly excited T_1 can lead to acetyl radicals which recombine only slowly to give a slow heat component, but no phosphorescence. There is no evidence for this mechanism in our experiments.

Pyridine

The opto-acoustic spectrum of this molecule has been discussed briefly in an earlier article,[5] and the highlights of that work are repeated here for completeness. In the region of overlapping $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ excitations of pyridine (2900–2300 Å), the in-phase opto-acoustic spectrum at 400 Hz shows barely resolvable vibrational structure for the $n \rightarrow \pi^*$ band and only a smooth profile for the $\pi \rightarrow \pi^*$ band. Because the out-of-phase signal is null at all wavelengths, the relaxation rates from the two states appear equal on our time scale, i.e., faster than ca. 10^6 sec^{-1}. If a small amount of biacetyl is added to this, then the out-of-phase spectrum becomes nonzero, but only in the region of pyridine $n \rightarrow \pi^*$ absorption, while the addition of oxygen to the pyridine–biacetyl mixture quenches this slow component of the heat. In pyridine, the $^1(n,\pi^*)$ state relaxes to $^3(\pi,\pi^*)$ with a modest quantum yield, and this triplet state can then energy transfer to the long-lived T_1 state of biacetyl. Wherever this happens in the spectrum, the radiationless heat will appear slowly. On the other hand, since the relaxation from the S_2 (π,π^*) state of pyridine remains fast in the presence of biacetyl, the S_2 state must relax via channels other than S_1 and T_1 and so probably internally converts to S_0 by way of relaxation.

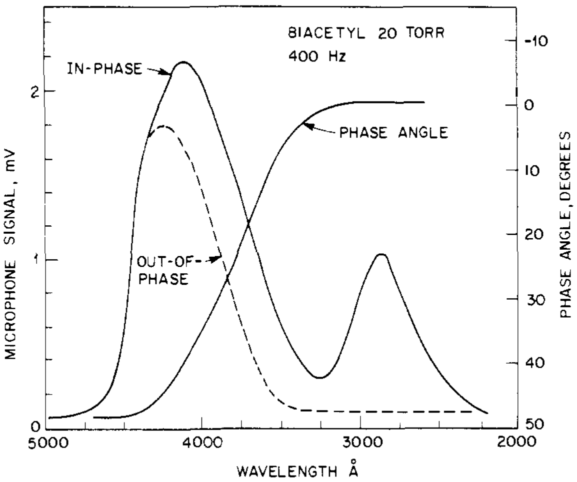

Figure 1. The in-phase and out-of-phase opto-acoustic spectra of biacetyl, taken with a phase angle chosen to extremize the S_2 signal. The curve labeled "phase angle" shows the angle at which the signal is nulled at each wavelength.

On measuring the phase angles across the spectrum, it is found that there is a 2° difference between the relaxations in the (n,π^*) and (π,π^*) regions of pyridine vapor (12 Torr), but that on adding 1.4 Torr of biacetyl, the difference increases to 5°. This increase of only 3° stands in strong contrast to the situation in, e.g., triazine, where the same concentration of biacetyl impedes the (n,π^*) relaxation by over 20°. The difference would seem to be in the rates of intersystem crossing; assuming that the energy transfer proceeds from the T_1 state of the donor, in pyridine, there is only a small quantum yield leading to the production of T_1; whereas in the diazines and triazine, this quantum yield approaches unity. Presuming that energy transfer to T_1 of biacetyl will introduce a phase lag of 45° (Figure 1) to an otherwise rapid relaxation (faster than 10^6 sec^{-1}), an increment of 3° implies that only 7% of the excited molecules are involved in energy transfer. This is not unreasonable since the intersystem crossing to T_1 in the (n,π^*) region of pyridine has a quantum yield of 0.14.[14] The corresponding phase-angle lag in benzene–biacetyl mixtures (benzene, 30 Torr; biacetyl, 0.4 Torr; nitrogen, 20 Torr) in a similar way leads to a figure of 25% of the excited benzene molecules eventually producing T_1 excitation in biacetyl.[5]

Pyrazine

There exists a considerable body of information on the electronic states of pyrazine which is of use in interpreting the opto-acoustic spectrum. The optical and opto-acoustic spectra are shown in Figure 2,[15] and it is clear from comparing the in-phase and out-of-phase intensities and band shapes that the relaxation rate is changing throughout the spectrum. This is confirmed by the phase-angle plot, shown below the optical and opto-acoustic spectra.

As in pyridine, there are in pyrazine $n \rightarrow \pi^*$ (S_1) and $\pi \rightarrow \pi^*$ (S_2) transitions, better separated here than in pyridine. The S_1 and S_2 states have the symmetries $^1B_{3u}$ and $^1B_{2u}$, respectively, and it has been shown that $^1B_{2u}$ character has been introduced into the lowest $^1B_{3u}$ state through the agency of a b_{1g} vibration.[16-18] Below S_1 in pyrazine, there are at least two triplets, the (n,π^*) triplet ($^3B_{3u}$) and a

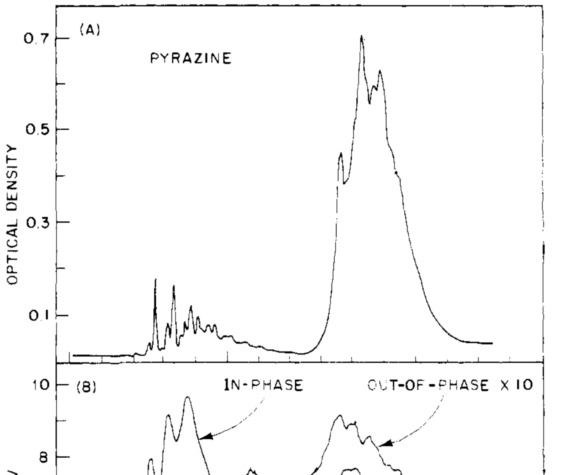

Figure 2. Spectral data on pyrazine vapor at 11 Torr: (A) the optical absorption spectrum; (B) the in-phase and out-of-phase opto-acoustic spectra at 400 Hz; (C) the phase-angle plot at 100 Hz.

(π,π^*) triplet ($^3B_{1u}$). In an absorption study of the pyrazine crystal, Hochstrasser and Marzzacco showed the two triplet states to be separated by only 1600 cm^{-1} with $^3B_{3u}$ lower.[19,20]

Intersystem crossing from S_1 to the T_1,T_2 manifold is very rapid (10^6 to 10^{11} sec^{-1})[8,21,22] with a triplet yield close to unity,[23] and El-Sayed estimates the spin-orbit-allowed $S_1(n,\pi^*) \rightarrow T_2(\pi,\pi^*)$ crossing to be 30 times more probable than the spin-orbit-forbidden $S_1(n,\pi^*) \rightarrow T_1(n,\pi^*)$ crossing.[22] The $T_2 \rightarrow T_1$ internal conversion is also a rapid process (ca. 10^{11} sec^{-1}).[8,22] By the same token, a spin-orbit stimulated crossing from either T_1 or T_2 to S_0 is symmetry forbidden so that, even though the sequence $S_1 \rightarrow T_2 \rightarrow T_1$ is quite rapid, the overall $S_1 \rightarrow S_0$ relaxation will be a slow one. This slow $T_1 \rightarrow S_0$ relaxation corresponds to the nearly constant phase angle observed in the 3300-2960 Å region. Using the observed phase-angle differences between the S_1 and S_2 excitations in eq 1, one estimates the overall relaxation from S_1 to require ca. 100 μsec, in fair agreement with a direct measurement of the T_1 lifetime of 63 μsec.[24]

All phosphorescence in pyrazine is observed by Frad et al.[24] to originate from the $v = 0$ level of T_1, and this then is the principal level leading to radiationless decay to the ground state. They also report that the $T_1 \rightarrow S_0$ radiationless decay rate is of the order of 10^7 sec^{-1} when 6000 cm^{-1} above the $v = 0$ level of T_1. However, under our conditions of a 10^8 sec^{-1} collision rate, these higher levels are apparently relaxed to $v = 0$ before they can decay to S_0. Thus the overall rate remains in the range of 10^4 sec^{-1}, limited by the T_1 ($v = 0$) $\rightarrow S_0$ intersystem crossing.

Note that this long-lived T_1 triplet state of pyrazine, which phosphoresces with a quantum yield of 0.30 in a glass at 77 K, has a phosphorescence quantum yield in the gas phase at room temperature of only 1×10^{-3} at 3 Torr.[9,25] Nakamura suggests that the T_1 lifetime in the gas phase is appreciably shortened by self-quenching, thereby decreasing the quantum yield.[25] One might therefore expect to see pressure effects on the S_1 phase angle, with high pyrazine pressures speeding the heat release from S_1. The phase angles in the S_1 region were studied using 0.2-10 Torr of pyrazine, and it was found that the S_1 relaxation is actually somewhat *slower* at the highest pressure, rather than faster. Inasmuch as Frad et al.[24] have measured the T_1 lifetimes in pyrazine and find no variation in the pressure range 0.2-10 Torr, we feel that the T_1 lifetime and $S_1 \rightarrow T_2 \rightarrow T_1 \rightarrow S_0$ radiationless rates are not influenced by self-quenching.

It is clear that a new relaxation mode appears in the S_1 band of pyrazine at ca. 2960 Å. First, perusal of the absorption spectrum under moderate resolution shows that the sharp bands above this wavelength become noticeably broader at this point. We also see that the phase angle for S_1 relaxation starts to decrease at this point and that, when pyrazine is mixed with biacetyl, only the wavelength region from 3300 to 2960 Å transfers to the T_1 state of biacetyl (vide infra). Thus a new channel does open up at 2960 Å which speeds somewhat the $S_1 \rightarrow S_0$ relaxation.

According to the ab initio calculations of Hackmeyer and Whitten[26] and of Wadt and Goddard,[27] the new level at 2960 Å in pyrazine would be the (n,π^*) triplet, $^3B_{2g}(T_3)$. Since the $S_1 \rightarrow T_3$ intersystem crossing is forbidden by spin-orbit coupling, but $T_3 \rightarrow S_0$ is allowed, it is not surprising that relaxation from this region of S_1 is only marginally faster than that from the low-wavelength region. The very clear break in the phase angle at 2960 Å observed when chopping at 100 Hz is far less obvious when this rate is increased to 400 Hz.[28] Since the new channel for relaxation at this point returns the molecule to the ground state while avoiding the S_1,T_1,T_2 set, the quantum yields for luminescence from these levels should be depressed for excitation beyond 2960 Å. Indeed, it is reported that both the emission quantum yield and the triplet yield in pyrazine suffer a strong reduction in the 2900-2700 Å region.[9,23]

Alternatively, Hochstrasser and Marzzacco[20] infer that a second, forbidden $n \rightarrow \pi^*$ band falls on top of the allowed $S_0 \rightarrow S_1$ band, their separation being 500-1500 cm^{-1} in the crystal. Wadt and Goddard's calculation does give a forbidden $^1A_g \rightarrow {}^1B_{2g}$ ($n \rightarrow \pi^*$) band as degenerate with $S_0 \rightarrow S_2$ ($\pi \rightarrow \pi^*$), but this is calculated to be 9000 cm^{-1} above $S_0 \rightarrow S_1$. The large splitting of the lone pair orbitals and also of the π MO's in pyrazine[29] make it difficult to see how the two lowest $n \rightarrow \pi^*$ bands could be as close as 1000 cm^{-1}. The incipient rise of phase angle at 3070 Å in Figure 2 agrees (fortuitously?) with the onset of faint broadening claimed by Hochstrasser and Marzzacco in the crystal spectrum.

Once the absorption into S_2 commences at ca. 2750 Å, the relaxation rate speeds up considerably, reaching a maximum at 2250 Å. In order to accommodate this fact, we must turn again to the calculations, which place a number of other states in the region of S_2. Among them is $T_4(n,\pi^*\ {}^3A_u)$, which should be reached from $S_2(\pi,\pi^*\ {}^1B_{2u})$ rather rapidly since it is spin-orbit allowed and is between (π,π^*)

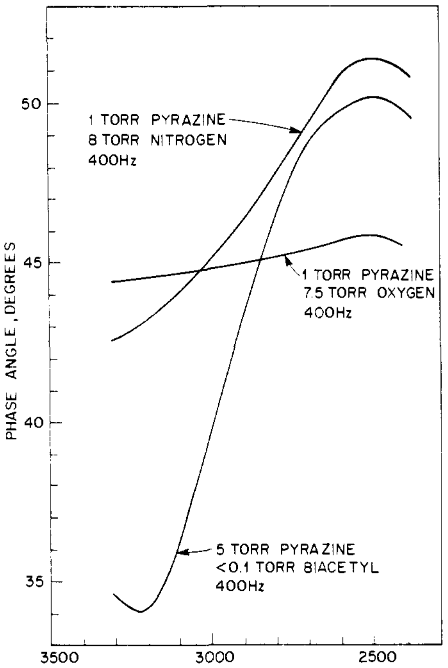

Figure 3. Phase-angle plots for pyrazine vapor mixed with nitrogen, oxygen, and biacetyl, all at 400 Hz.

and (n,π*) configurations. However, $^3A_u \rightarrow S_0$ is forbidden, and so one must make the ad hoc postulate that $^3A_u(T_4)$ internally converts rapidly to $^3B_{3g}(T_3)$, which then is able to relax rapidly to the ground state with the help of spin-orbit coupling. The two intersystem crossing steps in this chain obey both the (n,π*) ↔ (π,π*) and parity rules for strong spin-orbit coupling. The proposed chain of events avoids relaxation into the S_1,T_1,T_2 manifold from the S_2 region, which is consistent with the fact that virtually no fluorescence or phosphorescence follows from S_2 excitation.[9,25]

The rate of relaxation within S_2 increases up to 2500 Å, at which point it maximizes, and the behavior from this point to 2300 Å depends then upon the pressure of pyrazine. At pressures of 0.5-1.5 Torr, there is an essentially constant phase angle from 2500 to 2300 Å (Figure 3); whereas in the same region of pyrazine at 8-10 Torr, the null phase angle again decreases rapidly indicating a slower rate. The addition of 8 Torr of nitrogen to 1 Torr of pyrazine still gives the low-pressure phase-angle behavior. Possibly the increased excited state lifetime at high pressures is due to excimer formation. In any case, it is clear that another relaxation channel opens up at 2550 Å in pyrazine vapor.

It is well known that molecular oxygen is very efficient in general in quenching phosphorescence, there being several different mechanisms whereby it can shorten the T_1 lifetime.[30] In the opto-acoustic spectrometer, the effect of oxygen on pyrazine should be to accelerate the slow processes passing through the $T_1 \rightarrow S_0$ bottleneck. In Figure 3, there is shown a comparison of the phase-angle behaviors of 1 Torr of pyrazine in the presence of 8 Torr of nitrogen and the same pressure of oxygen. Clearly, the effect of oxygen is to make the rates of the slowest and fastest heats nearly equal, in contrast to the excitations in the presence of nitrogen, which relax about as they do in pure pyrazine vapor, Figure 2. From the point of view of the amplitude spectra at constant phase angle, the pyrazine spectrum in the presence of oxygen is totally in-phase. The addition of *cis*-butene-2 to pyrazine also resulted in an opto-acoustic spectrum of constant phase angle. The strong effect of oxygen on the relaxation of the pyrazine S_1 and/or T_1 states may be due to a chemical reaction in the excited state forming the *N*-oxide. Clearly, this rapid relaxation of the T_1 state by oxygen and *cis*-butene-2 should decrease the quantum yield of luminescence in pyrazine, and Frad et al. do report that oxygen quenches the $T_1 \rightarrow S_0$ phosphorescence,[24] while Nakamura reports a similar result for *cis*-butene-2.[25]

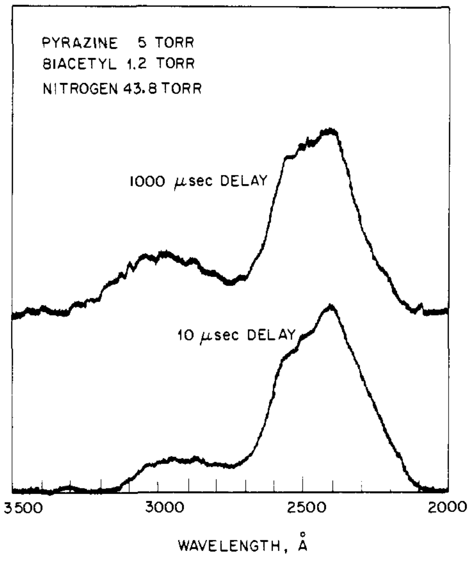

Figure 4. Opto-acoustic spectra of pyrazine vapor recorded 1000 and 10 μsec after the optical flash.

In direct contrast is the result of adding a trace of biacetyl (<0.1 Torr) to pyrazine vapor (5 Torr)[31] (Figure 3). In this case, the difference between the slowest and fastest relaxation is emphasized, the phase angle difference increasing from 10 to 16°. What we have here is the following: the lifetime of T_1 of pyrazine by itself is long, but not as long as that of biacetyl. In the long-wavelength region of S_1 absorption of pyrazine, there is rapid $S_1 \rightarrow T_2 \rightarrow T_1$ relaxation followed by energy transfer to the long-lived T_1 state of biacetyl. Consistent with this, we observe visually that the bright-green biacetyl phosphorescence is stimulated only in the 3280-2940 Å region of pyrazine. That the luminescence action spectrum does not continue beyond 2940 Å in the S_1 band of pyrazine shows that; since this is the threshold for intersystem crossing to T_3; the T_3 level does not energy transfer to T_1 of biacetyl nor does it relax via the T_2,T_1 manifold of pyrazine, but rather relaxes rapidly via $T_3 \rightarrow S_0$, as postulated above. Applied to S_2 of pyrazine, the same arguments show that S_2 avoids T_1 and T_2 in its relaxation, also in agreement with our earlier conclusions. Jones and Brewer[23] have also studied the pyrazine-to-biacetyl energy transfer by monitoring the latter's phosphorescence with a photomultiplier tube. They found that, in the 2670-2520 Å region, the energy transfer was slight but measurable.

The kinetic implications of the phase-angle plot for pyrazine-biacetyl mixtures is more readily demonstrated using a slightly different type of opto-acoustic spectrum. In this experiment, a flash lamp (3 J, 10 Hz) is used to excite the gas mixture, and the microphone signal is fed into a boxcar integrator; using a gate width of 100 μsec, the spectrum is scanned after a preset time delay. The spectra in the S_2 region are virtually identical after time delays of 1000 and 10 μsec (Figure 4) whereas, in the S_1 region, the signal is low after a 10 μsec delay, but much stronger after a 1000 μsec delay. In the S_1 band, the differences between these spectra are largest in the 3200-2800 Å region. It is clear from this that the release of heat from S_2 is rapid on the scale of 10-1000 μsec, but that the overall S_1 heat of pyrazine in the presence of biacetyl develops in this time domain, just as one would expect from the phase-angle plots of Figure 3.

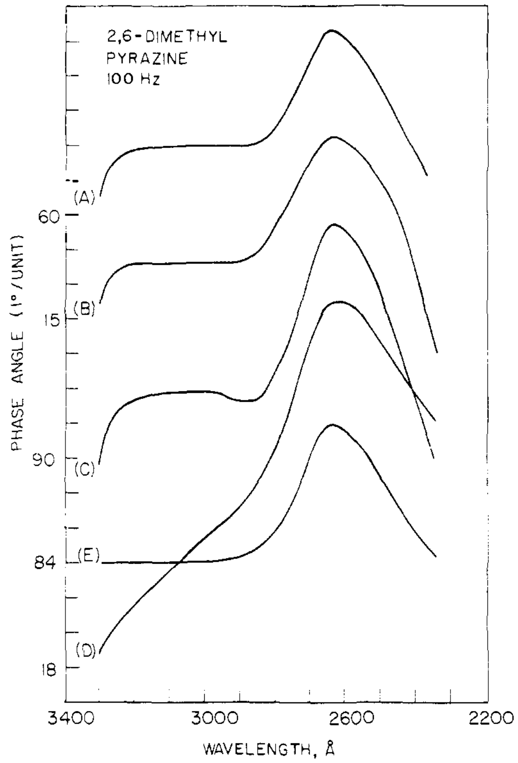

Figure 5. Phase-angle plots for 2,6-dimethylpyrazine taken at 100 Hz: (A) pure vapor at 1.9 Torr; (B) 60 Torr of nitrogen added to A; (C) 5 Torr of oxygen added to A; (D) less than 0.1 Torr of biacetyl added to A; (E) 2 Torr of oxygen added to D.

Methylpyrazines

In 2,6-dimethylpyrazine, rather different relaxation behavior is found, even though the absorption spectra of pyrazine and its 2,6-dimethyl derivative are expected to be very much alike. Several phase-angle plots are shown in Figure 5, and we would like to point out the dissimilarities between these and those of pyrazine. In the dimethyl compound, the relaxation from S_1 changes its phase angle at 2900 Å, but this would seem to be the S_2 threshold rather than T_3 as in pyrazine. Also, the capacity to transfer energy to the T_1 state of biacetyl extends only to the T_3 threshold in pyrazine whereas, in the dimethyl derivative, the characteristic green glow commences at 3330 Å and continues far into the S_2 region (2550 Å). Thus it would seem that S_2 relaxes via T_1 in this dimethyl derivative. Whereas the addition of biacetyl slows the S_1 relaxation in both pyrazine and 2,6-dimethylpyrazine (and oxygen returns the relaxation rate to its former value in the derivative), in pyrazine, both oxygen and *cis*-butene-2 will noticeably speed the relaxation in the S_1 region of pyrazine, but not in 2,6-dimethylpyrazine.

The peculiar behavior of the 2,6-dimethylpyrazine relaxation may be related to other peculiarities in the spectrum of this molecule. First, Moomaw et al. have analyzed the $S_0 \rightarrow S_1$ absorption band of this material and conclude that there are two $n \rightarrow \pi^*$ bands intimately overlapped in the S_1 region.[32] Second, Hochstrasser and Marzzacco conclude that T_1 and T_2 are separated in this compound by only 200 cm^{-1}, and that each is a mixture of (n,π^*) and (π,π^*) configurations.[20] This mixing is also evident in the phosphorescence-microwave double resonance spectrum of the compound in a *m*-xylene host crystal.[33]

The relaxation behavior of 2,6-dimethylpyrazine was observed to be distinctly different from that of pyrazine, and it was suggested that this might be due to the near-degeneracy of the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ configurations. Tetramethylpyrazine is interesting then, for in it, the $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ levels are further shifted so that the latter is now the lowest triplet configuration.[20,34] However, since the splitting is only 1900 cm^{-1} in the crystal, the T_1 and T_3 levels may also be strongly mixed in this compound.

Empirically, it is known that the phosphorescence lifetimes are much longer for (π,π^*) configurations compared with (n,π^*), and so one expects that S_1 and S_2 would relax at very different rates in tetramethylpyrazine, with that from S_1 being very slow. Consistent with this, the phosphorescence lifetime for tetramethylpyrazine in a matrix at 4.2 K is 0.41 sec.[34] No quantum yield is mentioned, but it seems safe to conclude that there are no rapid relaxation routes for T_1 in this molecule. The gas-phase opto-acoustic spectrum seems not to be interpretable in this way, however.

The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption bands in the tetramethylpyrazine spectrum are badly overlapped and, because of this, the phase-angle plot varies smoothly, without any abrupt change of angle on going from S_1 to S_2. Starting at its lowest point at 3100 Å, the phase angle rises only 4° (100 Hz) to a maximum at 2750 Å and then changes little from there to 2450 Å. As mentioned above, such a small change of phase angle is unexpected. It may be that in this molecule in the gas phase, the rates are not dictated solely by symmetry, or that the S_1 and S_2 bands are so badly overlapped that we are seeing only an average of the two vectors representing the heats.

Since relaxation from S_2 is generally a rapid process in compounds of this type, one is led to think that the S_1 relaxation also is rather rapid (but slower than 10^6 sec^{-1}). It is easiest to see this experimentally by again adding a small amount of biacetyl and measuring the relative phase angles between the S_1 band of biacetyl and the S_1 and S_2 bands of tetramethylpyrazine. From this, it is found that the 4° difference becomes 14° in the presence of biacetyl, indicating that S_1 of tetramethylpyrazine is able to energy transfer, but S_2 is not, and that S_2 is 36° faster than the slowest point in the S_1 band of biacetyl. Since we also measure a 45° phase-angle difference between the slowest part of the S_1 band of biacetyl and the most rapid relaxation ($>10^6$ sec^{-1}) in this compound, it is clear that the S_2 band of tetramethylpyrazine is relaxing at a rate approximating 10^6 sec^{-1}. The 4° phase lag for the S_1 band then yields a relaxation rate of 1×10^5 sec^{-1} for this spectral region.

Since biacetyl does have a large effect on the S_1 phase angle, it can be assumed that S_1 in tetramethylpyrazine is relaxing in large part via the triplet manifold, rather than by internal conversion. Visually, the biacetyl phosphorescence sensitized by tetramethylpyrazine is excited from 3080 to 2570 Å, just the region of $S_0 \rightarrow S_1$ absorption after deconvolution from the overlapping $S_0 \rightarrow S_2$ band.

Pyrimidine

The optical spectrum of pyrimidine (Figure 6) closely resembles that of pyrazine (Figure 2), there being a weak $n \rightarrow \pi^*$ band centered at ca. 2900 Å and a more intense $\pi \rightarrow \pi^*$ band centered at ca. 2400 Å. In the C_{2v} symmetry of this molecule, S_1 has symmetry $^1B_1$, and S_2 is $^1B_2$. The lowest triplet state is that corresponding to the (n,π^*) configuration, and Shimada suggests that the triplet corresponding to the $S_3(\pi,\pi^*)$ level (T_2) is just above T_1.[35] Indeed, using direct $S_0 \rightarrow T_x$ absorption in the pure crystal, Hochstrasser and Marzzacco deduce the presence of T_2 900 cm^{-1} above T_1 in pyrimidine. If true, this makes the analogy with the excited-state energy ladder of pyrazine a very good one. As with pyrazine, one again sees from the in-phase and out-of-phase opto-acoustic spectra that the overall radiationless relaxation rate is varying across the spectrum. Further, on running the phase-angle plot of pyrimidine at 100 and 400 Hz, a behavior is found which is rather like that of pyrazine, with the relaxation being slow in the n → π* region, and then speeding up by 5-10° in the π → π* region. A more precise measurement of the phase angle proved impossible for us, because pyrimidine had an adverse effect on the microphone foil which caused drifting and eventual loss of the signal. Taking a mean value of 8° between the slow S_1 and fast S_2 regions at 400 Hz gives a mean relaxation time of 60 μsec for the S_1 region.

Pursuing the analogy with pyrazine, in the S_1 excitation of pyrimidine, there is a rapid spin-orbit-allowed intersystem crossing to $T_2(\pi,\pi^*)$, the symmetry of which ($^3A_1$) forbids a spin-orbit assisted relaxation to the ground state. More likely, $^3A_1$ undergoes rapid internal conversion to $^3B_1(n,\pi^*)$, which then has an allowed intersystem crossing to S_0. This scheme differs from that for pyrazine only in that the last step is forbidden in the higher symmetry of pyrazine but is formally allowed in pyrimidine.

The behavior of pyrimidine (10 Torr), in the presence of a trace of biacetyl (0.1 Torr), is much like that of pyrazine. In this case, the heat from S_1 becomes very slow in the 3300-3100 Å region, then speeds to a maximum rate at 2800 Å, and is constant then from there to 2350 Å (the S_2 region). On adding a small amount of biacetyl to pyrimidine, the slowest point in the S_1 region of pyrimidine is some 20° behind the fastest in the S_2 region. However, in the same samples, we can also measure the biacetyl S_1 phase angle and find it to be 45-50° behind the fastest point in the S_2 region. Thus the overall S_1 relaxation rate decreases on adding biacetyl, but it does not become nearly as slow as in biacetyl itself.

The bright-green $T_1 \rightarrow S_0$ phosphorescence of biacetyl is observed when irradiating pyrimidine in the S_1 band up to 2800 Å. Apparently excitation into S_1 of pyrimidine is followed by intersystem crossing leading eventually to T_1 only up to 2800 Å. Notice also that the vibronic structure in the S_1 band of pyrimidine washes out in the 2750-2850 Å region. This behavior parallels quite closely that in the S_1 band of pyrazine, where it was concluded that the change of character part way through the band was due to the presence of the T_3 level. By analogy, it is suggested that the T_3 threshold in pyrimidine comes at 2800 Å. Hochstrasser and Marzzacco have also commented on the onset of broadening in the pyrimidine S_1 band and thereby infer the presence of a second n → π* band having an origin at ca. 2930 Å.

If oxygen (ca. 30 Torr) is added to pyrimidine, the phase angle becomes constant over the entire spectral region, illustrating the rapid quenching of all excited states by this gas.

Pyridazine

Judging from the preceding discussion, it is logical to expect the n → π* and π → π* bands in pyridazine to relax at different rates, with the latter relaxing perhaps an order of magnitude faster than the former. Instead, it is found that at both 100 and 400 Hz, there is a constant phase angle across the n → π* band which rises by only 1° at ca. 3000 Å and remains at that level across the π → π* band. As regards possible states involved in the relaxations, Hochstrasser and Marzzacco[20] have observed the direct excitations into the triplet manifold, and they conclude that the lowest triplet has the (n,π^*) configuration, with the (π,π^*) triplet coming at least 3000 cm^{-1} higher.

Unlike the situation in pyrazine, in the C_{2v} symmetry of pyridazine the spin-orbit matrix element between the lowest (n,π^*) triplet ($^3B_1$) and the ground state ($^1A_1$) is nonzero, and so the slow $T_1 \rightarrow S_0$ step in pyrazine may be much faster in the lower symmetry. Such an argument could explain the rapid relaxation from S_1 if it were known that pyridazine followed the $^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*) \rightarrow {}^3(n,\pi^*) \rightarrow S_0$ chain appropriate for pyrazine.

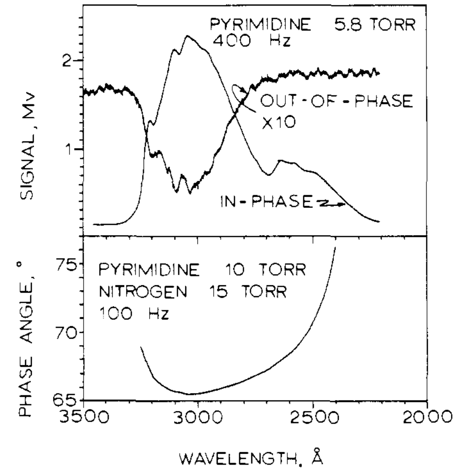

Figure 6. In-phase and out-of-phase opto-acoustic spectra of pyrimidine (upper) and the phase-angle plot (lower).

Pyridazine is abnormal in its response to the addition of a small amount of biacetyl. We find that there is no change of phase angle in the pyridazine S_1-S_2 region upon adding biacetyl, nor does irradiation in the S_1-S_2 region yield the characteristic green phosphorescence indicative of energy transfer to T_1 of biacetyl. Possibly the $T_1 \rightarrow S_0$ relaxation in pyridazine is too rapid to allow energy transfer to biacetyl.

sym-Triazine

The absorption spectrum of *sym*-triazine is rather different from those of the diazines; there is an intense n → π* band centered at 2700 Å, followed by a much weaker π → π* band at 2150 Å.[36] Only the first of these is observed in the opto-acoustic spectrum. Under moderate resolution (Cary 15 spectrophotometer), the n → π* band of *sym*-triazine shows several sharp vibronic features which broaden somewhat at ca. 2700 Å and smear out totally at ca. 2550 Å, indicating the presence of other states at these wavelengths. None of the vibronic structure is observed in the opto-acoustic spectrum (Figure 7) but, in the phase-angle plot, there is a break at 2700 and another at 2500 Å, indicating the presence of new channels for relaxation at these wavelengths. However, the phase angle spans a range of only 1-2°, illustrating an almost identical overall relaxation rate across the S_1 band; similar phase-angle plots were obtained at 100 and 400 Hz chopping frequencies. It seems more likely that we have triplet states at 2700 and 2500 Å, but the presence of other n → π* excitations cannot be ruled out. Indeed, Brinen and Goodman[37] have studied the $S_0 \rightarrow S_1$ absorption band of *sym*-triazine and assign the sharp structure to the allowed n → π* band, $^1A'_1 \rightarrow {}^1A''_2$, and the broad portion of the band to n → π*, $^1A'_1 \rightarrow {}^1E''$.

Most interesting is the effect of adding a small amount of biacetyl to *sym*-triazine. In this case, a bright-greem emission ($T_1 \rightarrow S_0$ in biacetyl) results from irradiating the triazine in the region from 3230 to 2500 Å, and the phase-angle spans a range of over 20°. In the figure, one sees the rapidly rising relaxation rate of the S_1 state of biacetyl in the 4500-3500 Å region, with the S_1 relaxation of the triazine then starting at 3250 Å. Its phase angle at this point is more than 20° below the fastest point in the spectrum (2550 Å), compared with 2° below the fastest point in the spectrum without biacetyl. Clearly then, the front part of the $S_0 \rightarrow S_1$ band is very active in energy transfer to T_1 of

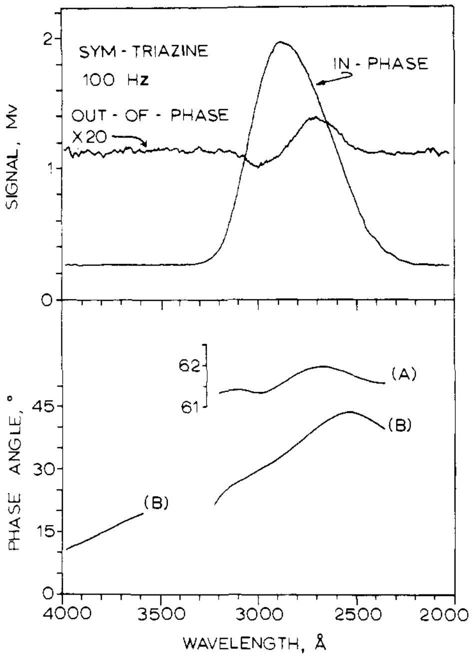

Figure 7. In-phase and out-of-phase opto-acoustic spectra of *sym*-triazine (8 Torr) at 100 Hz (upper) and phase-angle plot without biacetyl (A) and with 1 Torr of biacetyl added (B) (lower).

biacetyl, yielding an overall slow relaxation rate, while the overall rate quickens as one scans through the band toward 2500 Å. The increasing rate implies either that the transfer efficiency decreases as one moves through the S_1 band, or that transfer to T_2 of biacetyl becomes more important as one moves through the S_1 band. The strong effect of biacetyl is completely removed by the addition of 10 Torr of oxygen, as expected. The lowest triplet state of triazine is $^3(n,\pi^*)$,[37] and this is probably the state which transfers to T_1 of biacetyl.

If we could observe the heat from S_2, which is presumably very fast, we could then see how many degrees slower is the heat from S_1 and from that estimate its lifetime. However, we cannot get enough signal at S_2 for a measurement. Such a measure can be obtained instead by comparing the phase angle at the short-wavelength part of the $S_0 \rightarrow S_1$ band with the slow-heat phase angle from the S_1 band of biacetyl (Figure 7). From this, it is seen that the back part of S_1 in *sym*-triazine is 40° faster (at 100 Hz) than the S_1 relaxation in biacetyl; i.e., the S_1 and S_2 relaxations of *sym*-triazine in the absence of biacetyl are both rapid (at least 10^6 sec^{-1}).

sym-Tetrazine

Because Vemulapalli and Cassen[38] find the fluorescence quantum yield of *sym*-tetrazine to be only 0.01-0.05 when extrapolated to zero pressure, it is clear that radiationless decay must be important in the first excited singlet state ($^1B_{3u}$).[39] McDonald and Brus[40] studied this using laser excitation at four wavelengths within the S_1 band (5514, 5326, 4766, and 4602 Å) and found a $^1B_{3u}$ lifetime of less than 100 nsec, while Wiersma reports a value closer to 1 nsec.[41] Rather than relaxing to $^3B_{3u}$ which does not have a sufficient density of levels to promote a rapid intersystem crossing, McDonald and Brus instead conclude that $^1B_{3u}$ relaxes by internal conversion to the ^1A_g ground state. Our opto-acoustic results can be understood within this framework and simultaneously extend the data.

When chopped at 400 Hz, the three excitations to S_1, S_2, and S_3 of the optical spectrum[1] appear at their expected positions in the in-phase opto-acoustic spectrum [Figure 8 (upper)]. The out-of-phase spectrum, when expanded ×10, is null at all wavelengths as closely as can be determined, demonstrating that all points within the S_1, S_2, and S_3 bands relax at the same rates, i.e., at or faster than our response time of ca. 10^{-6} sec. The spectra are unchanged in the presence of 20 Torr of O_2. We have also tried to introduce a slow component into the *sym*-tetrazine spectrum by adding a large excess of biacetyl [Figure 8 (lower)]. Here it is seen that S_1 and S_3 of *sym*-tetrazine are nulled when the S_2 band of biacetyl is nulled, showing that relaxation from all three of these states is equally rapid on our time scale. On the other hand, relaxation from S_1 of biacetyl retains an intense out-of-phase component since it remains slow. The lack of effect of biacetyl on *sym*-tetrazine is reasonable on several counts: first, the tetrazine is relaxing at approximately the collision rate in our experiment; and second, the transfer to T_1 of biacetyl would occur most readily from the lowest triplet of tetrazine, whereas this state is not in the relaxation chain from S_1. Note also that most of the S_1 band of *sym*-tetrazine is below the S_1 and T_1 levels of biacetyl. In contrast to the behavior of biacetyl in tetrazine, the slow S_1 band of pyrazine becomes fast in the presence of *sym*-tetrazine, suggesting an energy transfer in this case.

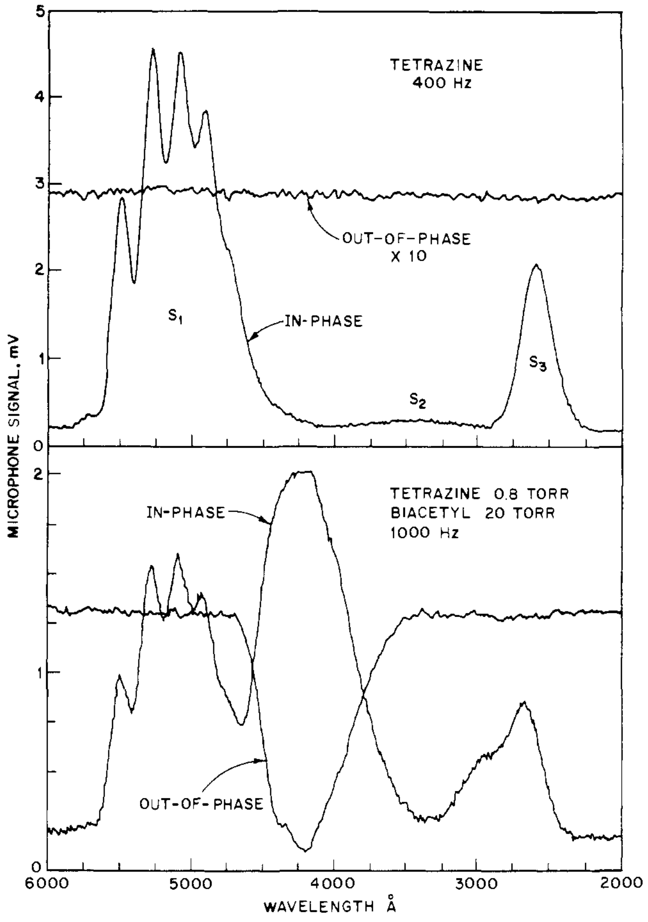

Figure 8. In-phase and out-of-phase opto-acoustic spectra of *sym*-tetrazine vapor at 400 Hz (upper) and at 1000 Hz with biacetyl added (lower).

Acknowledgment. It is a pleasure to acknowledge several conversations with Louis Brus and his generous gift of *sym*-tetrazine. We are indebted as well to the referee for a critical reading of the manuscript.

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Triplet-Sensitized Cis–Trans Isomerization of the Protonated Schiff Base of Retinal Isomers

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Received June 25, 1974

Abstract: Pulsed (N_2 laser) and continuous excitation methods are applied to ethanol solutions of the protonated Schiff bases of retinal isomers (PRSB). PRSB's triplet states, produced via energy transfer from the triplet state of phenanthrene, are found to undergo cis-trans isomerization processes. The observed yields of the triplet-sensitized isomerization ($\phi^T{}_{ISO}$) for the 9-cis, 13-cis, 11-cis, and all-trans isomers are, respectively, 0.5 ± 0.2, 0.2 ± 0.1, 1.0 ± 0.2, and <0.05. The large yield for the 11-cis isomer is rationalized in terms of the destabilization of the first excited triplet of this isomer due to torsion around its 12–13 single bond. Calculations indicate that this leads to a substantial decrease in the barrier for twisting around the double bond and thus may be responsible for the exceptionally high $\phi^T{}_{ISO}$ value observed. The relevance of this analysis to the photochemistry of visual pigments is discussed.

It is generally accepted that, in visual pigments, 11-cis retinal is covalently bound to the protein opsin via a Schiff base linkage.[1] The large bathochromic shifts, relative to the retinal Schiff base (RSB) observed upon pigment formation, are not fully understood, but it now seems likely that they result from the formation of a protonated Schiff base (PRSB).[1d,2] Thus, the photochemical properties of PRSB's are of considerable interest since they may bear directly upon the 11-cis → all-trans photoisomerization that is believed to initiate visual excitation.[3]

Previous studies have considered the primary photophysical processes of molecules related to the visual chromophore. These include retinal,[4] RSB,[5] retinol,[6] retinyl acetate, retinyl-*n*-butylamine, and retinal oxime.[7] In the present work, we selectively populate the lowest triplet state of PRSB (previously undetected),[4a,b] via inter-molecular energy transfer from a triplet donor molecule, focusing our attention on isomerization processes in the triplet manifold of the acceptor. The experimental photosensitized isomerization yields are related to theoretically calculated energy barriers in the lowest triplet state.

In carrying out the theoretical calculations, we have been interested primarily in the specific effects introduced by the twisting in the polyene chain of the 11-cis isomer, where the major deviation from planarity involves significant torsion about the 12–13 single bond (dihedral angle θ_{12-13}).[2,8–11] The fact that the 11-cis isomer is a highly twisted molecule has been used to interpret spectroscopic results[8,12,13] but has not been considered in previous calculations of barriers to isomerization of retinals and related molecules.[12,14,15] In this study, we calculate the effect of this twisting on the potential energy surfaces of the lowest triplet states of PRSB. It is shown that our photosensitization data may be rationalized in terms of this effect.

Experimental Section

All-trans, 9-cis, 13-cis (Sigma Chemical Co.), and 11-cis retinal (a gift from Hoffmann-La Roche, N.J.) were used without further purification. The corresponding Schiff bases were prepared at room temperature by dissolving the aldehydes (~10^{-4} *M*) in *n*-butylamine (Fluka, puriss). Acidified ethanol (Fluka, spectrograde) solutions were prepared by evaporating the original *n*-butylamine solvent under a stream of nitrogen and dissolving the residual Schiff base in acidified (10^{-3} *M* $HClO_4$) ethanol. The ab-

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