

reasonable that the proton transfer reaction which triggers the subsequent reactions is facilitated by the compression, which must lower the potential barrier for the proton transfer as a result of the shortening of the N...O distances in the complex. This reaction mechanism under high pressure is illustrated schematically in Figure 13.

DMPD₅·CA₂. Though the changes of the spectra for this compound under high pressures are less than those for PPD·CA as is shown in Figures 8 and 9, it is most likely that some chemical reaction occurs under pressures above 40 kbar. In this case neither CA nor TCHQ is formed. This comparatively inert behavior may arise from the difference in reactivity between DMPD⁺ and PPD⁺ or from the fact that this compound is not a 1:1 complex as in PPD·CA.

TMPD·CA. In this case, the rise in resistance above

200 kbar is not as sharp as in the PPD·CA complex. Neither CA nor TCHQ is formed in this case. From the result of Figures 10 and 11 this complex does not show any intermediate reaction products but leads directly to final spectra as seen in the case of PPD·CA. This may come from the different chemical properties of TMPD⁺ which lacks active hydrogen atoms. Its lower reactivity is shown also in the fact that the rise in resistance begins at about 230 kbar and is not as sharp as in the PPD·CA complex, as is seen in Figure 7.

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Emissive Characteristics of Amidic Molecules^{1a}

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Abstract: Simple amides and various closely related molecules are nonemissive at 77°K. Planar oxamides, however, do phosphoresce and the investigation of oxamidic T₁ states leads to the following conclusions concerning the T₁ state properties of simple amides. (i) The T₁ state is of ³Γ_{ππ*} type. (ii) This ³Γ_{ππ*} state is nonemissive. (iii) The energy of this state is 36,000 ≤ E(³Γ_{ππ*}) ≤ 38,500 cm⁻¹. (iv) The ¹Γ_{ππ*} - ³Γ_{ππ*} energy separation is ~15,000 cm⁻¹. The emissive characteristics of amide-containing molecules (*i.e.*, amides, ureas, oxamides, parabanic acids, acylureas, etc.) are reported and are diverse; this diversity may be rationalized in terms of the following triplet state properties. (v) A T₁ state of ³Γ_{ππ*} type is nonemissive. (vi) A T₁ state of mixed ³Γ_{nπ*}/³Γ_{ππ*} type is emissive, possesses a weak to moderate intensity output, is usually structureless, and exhibits a decay lifetime of ~10⁻² sec. (vii) A T₁ state of ³Γ_{nπ*} type is strongly emissive, exhibits vibronic structure involving a dominant C=O stretching mode, and possesses a decay lifetime of ~10⁻³ sec. The nature of the T₁ state (*i.e.*, whether ³Γ_{ππ*}, ³Γ_{nπ*}/³Γ_{ππ*}, or ³Γ_{nπ*}) is determined by the interactions of an amide group with various other chromophoric groupings including the amide group itself; these interactions may lead to preferential stabilizations of amide ^{1,3}Γ_{nπ*} or ^{1,3}Γ_{ππ*} parent states and, hence, to the observed diversity of emissive properties. The energy difference between ¹Γ_{ππ*} and ¹Γ_{nπ*} states is useful in predicting emission behavior for amidic T₁ states. The consequences of these conclusions for the T₁ state of the peptide linkage are discussed.

The importance and prevalence of the peptide bond in biological systems is well known. However, its function in electronic energy-transfer and energy-degradative events is unclear, apparently because the experimental characterization of the lower energy excited states of the peptide linkage has proven to be exceedingly difficult. Some of the lower energy excited electronic states of the singlet manifold are known, at least to the extent of energy, intensity, and, possibly, orbital-excitation nature. In contrast, neither the orbital-excitation nature nor energy of the T₁ state is available.

The deposition of energy in various excited states of the peptide linkage is surely (by virtue of the ubiquity of this unit in the protein and enzyme primary structures) one of the secondary, or even primary, events in radiation biology. Since the peptide T₁ state is one of the

end results of such a deposition, it follows that the nature of this latter state is of some concern.

Our previous attempts^{2,3} to characterize the orbital-excitation nature and energy of the T₁ state of the peptide linkage were hampered by a confusing literature about the emissive properties of peptide-related molecules. Our prior approaches were of two types: (1) a survey² of the excited electronic state properties of molecules which are isoelectronic with the peptide unit (*i.e.*, O₃, NO₂⁻, HCOO⁻, HCOOCH₃, HCONH₂, etc.) and the devisement of theoretical algorithms which enabled us to interrelate the excited state characteristics of these compounds and to extrapolate them to the peptide linkage; (2) an extensive study of amide-substituted aromatic compounds³ in which the emissive energies and

(1) (a) Research supported by contract between The United States Atomic Energy Commission-Biology Branch and The Louisiana State University; (b) National Science Foundation Fellow (Fellowship No. 40041).

(2) (a) H. J. Maria, D. B. Larson, M. E. McCarville, and S. P. McGlynn, *Accounts Chem. Res.*, **3**, 368 (1970); () S. P. McGlynn, H. J. Maria, and D. B. Larson, "Organic Scintillators and Liquid Scintillation Counting," D. Horrocks, Ed., Academic Press, New York, N. Y., 1971, p 201.

(3) H. J. Maria and S. P. McGlynn, *J. Chem. Phys.*, **52** 3399 (1970).

lifetimes were used in an attempt to evaluate the state energies and lifetimes of the amide subunit through two perturbative approaches,³ both of which were found to be inadequate.

The present effort presents a systematic study of the emissive properties of simple *amidic* compounds including the simple amides. In contrast to the prior work, however, we now present a resolution to the T_1 characterizations of amides utilizing a composite-molecule view of amide-containing molecules. We provide a discussion of the emissive parameters of such molecules, we relate these parameters to the nature of the T_1 state in such amide-containing molecules and, finally, we ascertain the nature of the T_1 state of the isolated amidic residue. The congruence of the conclusions based on the isoelectronic, model compound serialization of ref 2, and the phosphorescence process identifications of the present work provide a validating cross check of the general correctness of these approaches.

(1) **An Amide Classification Scheme.** All molecules containing the $-C(=O)N<$ residue are considered to be amidic molecules. They may be divided into two major classes, *isolated amides* and *interactive amides*.

The *isolated amides* are characterized by the fact that the amide unit is bonded directly to methylene or other saturated groups. Examples are provided by the simple aliphatic amides and lactams. They may also contain more than one amide residue as in 2,5-diketopiperazine. Some members of this class are sketched in Figure 1A.

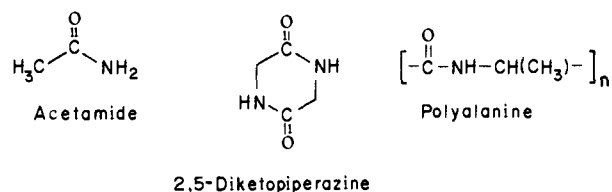
The *interactive amides* are characterized by the fact that the amide group is bonded directly to a perturbing residue such as carbonyl, an ethylenic system, or an amine group. This class of molecules is very diverse. Examples are provided in Figure 1B, where a further subclassification into *homointeractive*, *heterointeractive*, and *biinteractive* types is outlined. If the residue(s) bonded to the amide group is itself an amide unit, these molecules are said to be *homointeractive*. If the residue(s) with which the amide group interacts is not amidic, these molecules are said to be *heterointeractive*. And if the molecule contains both hetero- and homointeractive parts, it is said to be *biinteractive*.

(2) **Aims and Limitations.** A classification such as that given is valuable only insofar as it leads to a rationalization of the properties of amidic molecules in terms of the properties of amide units and the other subunits of the molecule with which they interact. In other words, the classification given implies an attempt to describe the excited state properties of complex amides in terms of a composite-molecule model. The utility of such an approach has already been demonstrated for certain homointeractive⁴ and biinteractive amides.⁵ Such success as was achieved^{4,5} was wholly dependent on the development of correlative techniques which, relative to experiment, provide an empirical description of pertinent excited states and which, relative to quantum-chemical computations, provide a means of relating the excited states of one molecule to those of others within the series of molecules under

(4) D. B. Larson and S. P. McGlynn, *J. Mol. Spectrosc.*, **47** 469 (1973).

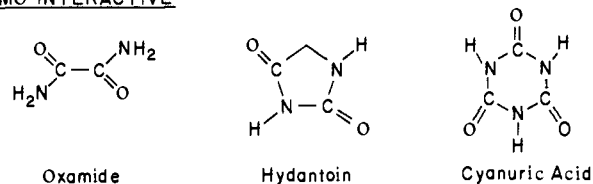
(5) D. B. Larson, J. F. Arnett, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **95**, 6928 (1973).

(A) ISOLATED AMIDES

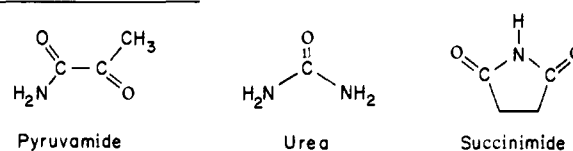


(B) INTERACTIVE AMIDES

HOMO-INTERACTIVE



HETERO-INTERACTIVE



BI-INTERACTIVE

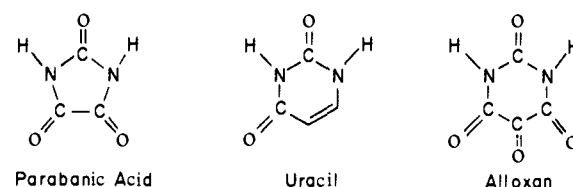


Figure 1. A classification scheme for amidic molecules.

investigation. This prior success prompts the present attempt at a greater generality.

The utility of any correlative approach increases as the amount of available empirical information increases. Thus, the singlet manifold of states is more easily handled than is the triplet manifold because (a) the only readily accessible triplet state, in an experimental sense, is the T_1 state and then only if the T_1 state is emissive, and (b) T_1 emissive properties not only depend critically on the orbital-excitation nature (*i.e.*, $n\pi^*$ or $\pi\pi^*$) of T_1 but also on the relative positions⁶ of other T_1 and even S_1 states. In addition to being emissive, the amides in question should also possess T_1 states of amidic character;⁷ in other words, the excitation in the T_1 state must possess dominant amplitude on the amidic center(s). This prerequisite eliminates such molecules as the aromatic amides, molecules for which extensive study⁸ indicates that the T_1 states are exclusively of ${}^3\Gamma_{\pi\pi^*}$ ring type and not much different from those of the parent aromatic molecules. A number of compounds which satisfy both criteria (*i.e.*, emissivity and

(6) D. N. Shigorin, *Russ. J. Phys. Chem.*, **44**, 1527 (1970).

(7) The reason for this stipulation is, simply, that our interest lies in the amidic T_1 state and not in ring states. The opposite approach, namely the study of ${}^3\Gamma_{\pi\pi^*}$ ring states perturbed by a ${}^3\Gamma_{\pi\pi^*}$ state of a substituent, has already been tried for aromatic carboxylic acids³ and amides⁹ and found to be of marginal use insofar as the provision of information on the ${}^3\Gamma_{\pi\pi^*}$ state of the appended group is concerned.

(8) Y. H. Lui, D. B. Larson, C. S. Seliskar, and S. P. McGlynn, to be submitted for publication.

Table I. Phosphorescence of Simple Amides and Related Compounds^{a-c}

Molecule	Preparative methods	Emission characteristics ^d
Acetamide	Multiply vacuum distilled; multiply crystallized/water	No emission
N-Methylacetamide	Multiply vacuum distilled; gas chromatographed; zone refined	Very weak emission; very dependent on wavelength of excitation
N,N-Dimethylacetamide	Multiply vacuum distilled	No emission
2-Chloroacetamide	Multiply crystallized/water	No emission; dissociates in solution
Thioacetamide	Multiply crystallized/water	Freshly prepared solutions show no emission; decomposes in solid and in solution
ε-Caprolactam	Used as purchased	No emission
2,5-Diketopiperazine	Vacuum sublimed	No emission
Alanine anhydride	Used as purchased	No emission
Urea	Multiply crystallized/methanol; vacuum sublimed; chromatographed on Al ₂ O ₃ column	Very weak emission; very dependent on wavelength of excitation
Thiourea	Multiply crystallized/water	Very weak emission; very dependent on wavelength of excitation
Biuret	Multiply crystallized/water	Very weak emission; very dependent on wavelength of excitation
Ethyl N,N-dimethylglycinate	Multiply vacuum distilled	No emission; decomposition upon irradiation
Lead glycinate	Multiply recrystallized/water-NaOH	Very weak emission; very dependent on wavelength of excitation

^a All of these emission studies refer to clear glassy solutions at 77°K. The solvents used were EPA (ethyl ether/ethyl alcohol/isopentane; 5:2:5), mixed alcoholic solvent (methyl/isopropyl/ethyl alcohol), and 3-methylpentane. Preliminary work indicated that degassing procedures did not instigate luminescence where none was previously observed and did not detectably alter the intensity of any luminescence which was previously observed. Hence, degassing was not used in all instances. ^b Relative to this tabulation, the criteria chosen to validate the presence of a phosphorescence intrinsic to the molecule of interest are: the intensity of the luminescence must be significantly (at least twice) above background emission; the emission spectrum must be independent of excitation wavelength; and the emission spectrum of a given molecule must not change with method of preparation, with method of purification, or with the source of the compound. ^c A number of authors have reported emissions which might be associated with the isolated amidic type of grouping. These are (1) P. Douzou and J. Franz, *J. Chim. Phys. Physiochim. Biol.*, **59**, 578 (1962); (2) H. Kallman, V. J. Krasnansky, and P. Person, *Photochem. Photobiol.*, **8**, 65 (1968); *Ber. Bunsenges. Phys. Chem.*, **72**, 340 (1968); (3) P. Wels, *Pflugers Arch.*, **219**, 738 (1928). (4) R. H. Steele and A. Szent-Gyorgyi, *Proc. Nat. Acad. Sci. U. S.*, **43**, 477 (1957); **44**, 540 (1958); (5) I. Isenberg and A. Szent-Gyorgyi, *ibid.*, **44**, 519 (1958); (6) E. Fujimori, *Biochim. Biophys. Acta*, **40**, 251 (1960). Of these, (2) is the only one which makes serious claims for an isolated amide emissivity. For the most part, 4-6 imply the role of species related to indole but do claim emissivity of systems in which indole is absent. While concentrating on proteins containing aromatic residues, (1) also reports an emissivity of systems in which such residues are absent. Clearly, we disagree with all implications of isolated-amide emissivities. ^d The observation "no emission" implies a quantum yield $\Phi_p \leq 10^{-4}$. The observation "very weak emission" implies $10^{-4} \leq \Phi_p < 10^{-3}$. The term "very dependent on wavelength of excitation" usually implies a shift of $+200 \leq \lambda(\text{emission maximum}) \leq +300 \text{ \AA}$ for a change of excitation wavelength from 2500 to 3000 Å. The luminescence maxima, where luminescence is observed, usually lie in the range 4000-4500 Å.

amidic T₁ nature) have been found, and a study of these molecules forms the basis of the present work. The purpose of the present work, then, is a discussion of the lower energy excited states of amidic molecules. Emphasis is placed on the T₁ state of these systems and the set of molecules of interest is restricted to those in which the lower energy excited states are amidic. The plan of the paper is as follows.

(i) A survey of the emissivity of isolated amides and the demonstration that the amide unit is either non-luminophoric or very weakly luminophoric.

(ii) A discussion of pertinent electronic absorption and emission properties of selected interactive amides (*i.e.*, oxamides, dithiooxamides, pyruvamide, oxamates, parabanic acids, etc.) and the interpretation of the observed properties.

(iii) An attempt to understand the nature of the lower energy excited states of isolated amides and their luminophoric properties in terms of our knowledge of interactive amides.

(iv) An attempt to provide a consistent correlation of the emissive properties of amidic T₁ states of a large number of diverse amide-containing molecules within the framework of a limited number of generalizations.

Experimental Section

Experimental details on the study of the isolated amides are incorporated in the text, particularly in Table I; details on the oxamides,⁴ parabanic acids,⁵ thiooxamides,⁹ ethyl oxamate,¹⁰ and

pyruvamide¹⁰ are included in the designated references. Hydantoin (Kodak), acetamide (MCB), acetylurea (K & K), and dihydrouracil (K & K) were purified by repeated recrystallization from either water or ethanol.

Diacetylhydrazine was prepared from hydrazine sulfate, sodium acetate, and acetic anhydride by the method of Peilizzari¹¹ and was purified by several recrystallizations from ethanol. A very weak absorption band ($\lambda_{\text{max}} \sim 285 \text{ m}\mu$, $\epsilon_{\text{max}} \sim 0.5 \text{ l. mol}^{-1} \text{ cm}^{-1}$) which was not removed by recrystallization but which did appear to diminish in intensity is ascribed to impurity. This conclusion is substantiated by the rather poor comparison of experimental and theoretical elemental analyses: Calcd: N, 24.6; C, 42.0; H, 5.3. Found: N, 22.4; C, 37.8; H, 6.9. It should be noted, however, that an early publication of Yamada and Tsuchida¹² on the polarized absorption spectrum of a diformylhydrazine single crystal also indicated a very weak absorption in the same 280-m μ region which we now ascribe to impurity.

The vapor spectrum of diacetylhydrazine was obtained on a McPherson 1-m v-uv double beam spectrometer in a 10-cm heated cell. Emission techniques have been described previously.^{4,5}

Results

(1) **Isolated Amides.** The results of an extensive study of the emission properties of relatively simple amides and some closely related molecules are given in Table I. The majority of these molecules are isolated amides; the others, for reasons to be discussed

(9) D. B. Larson, J. F. Arnett, and S. P. McGlynn, *Chem. Phys. Lett.*, **23**, 322 (1973).

(10) D. B. Larson, J. F. Arnett, and S. P. McGlynn, *J. Chem. Phys.*, to be submitted for publication.

(11) G. Peilizzari, *Gazz. Chim. Ital.*, **391**, 536 (1909).

(12) S. Yamada and R. Tsuchida, *J. Chem. Phys.*, **22**, 1629 (1954).

later, tend toward behavior characteristic of the isolated amides.

None of the listed molecules exhibit fluorescence. Additionally, the low-temperature glassy solutions of these substances are either nonphosphorescent or minimally phosphorescent. In these latter, weakly phosphorescent cases, the emission profiles and energies are sensitive functions of the exciting frequency, indicating that the luminescence may be of impurity origin. The luminescence decay times, where measurable, are generally rather long ($\tau_p > 0.1$ sec).

Since most of the molecules listed in Table I absorb¹³ at such very short wavelengths (${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition, $215 \text{ m}\mu < \lambda_{\text{max}} < 230 \text{ m}\mu$; and ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transitions, $180 \text{ m}\mu < \lambda_{\text{max}} < 203 \text{ m}\mu$) and since the xenon excitation source has a low photon output at $\lambda \leq 2500 \text{ \AA}$, some care must be taken to ensure adequate sample absorptivity (*i.e.*, to ensure moderate excited state densities). Consequently, all compounds were investigated at the highest concentration which, for a given solvent, led to a glass of good optical character at 77°K . Thus, some or all of the excitation-frequency dependence of the luminescence of the weak emitters might be attributed to either aggregation or protocrystallization effects. In this connection, some of these molecules in Table I have been studied in aqueous systems at 77°K , and we deem it significant that all are emissive. These aqueous systems are opaque, polycrystalline masses at 77°K and probably contain solute microcrystals. In general, the aqueous-system luminescences are very weak and extremely dependent on excitation wavelength. In the one case of ϵ -caprolactam, the emission spectrum ($\tau_p \simeq 1$ sec) was almost independent of exciting wavelength and relatively intense. However, since ϵ -caprolactam in true glassy solutions at 77°K does not emit, even at very high concentrations ($\sim 10^{-1} M$), it is probable that this latter emission is not due to any molecular phosphorescence process in ϵ -caprolactam itself. We assume, instead, that the frozen-water luminescence is attributable to some photochemically derived species or to an undetermined solid state defect emission act and that these observations vindicate our attribution of the luminescence to impurity sources.

We also deem it significant that neither chloroacetamide nor thioacetamide is emissive. Conditions in these two systems are most advantageous for luminescence: both have significant absorption at $\lambda > 250 \text{ m}\mu$, leaving no doubt that sufficient singlet populations are produced optically; and both provide an internal spin-orbit coupling perturbation which might be assumed to increase the probability of a $T_1 \rightarrow S_0$ process.

Our conclusions concerning the nonemissivity of simple amide systems concurs with that of Dearman, Lang, and Neely¹⁴ on *N,N*-diethylacetamide, *N*-ethylacetamide, *N,N*-di-*tert*-butylpropionamide, and *N*-propylpropionamide. Thus, our studies lead us to conclude that isolated amides are nonluminophoric. However, it is well to stress that the complete absence of simple amide luminescence is not essential to our arguments. All that is required, and all that we emphasize, is that the emissivity of such systems, if in fact it exists at all, is exceedingly weak (*i.e.*, $\Phi_p < 10^{-4}$).

(13) E. B. Nielson and J. A. Schellman, *J. Phys. Chem.*, **71**, 2297 (1967).

(14) H. H. Dearman, F. T. Lang, and W. C. Neely, *J. Polym. Sci.*, **7**, 497 (1969).

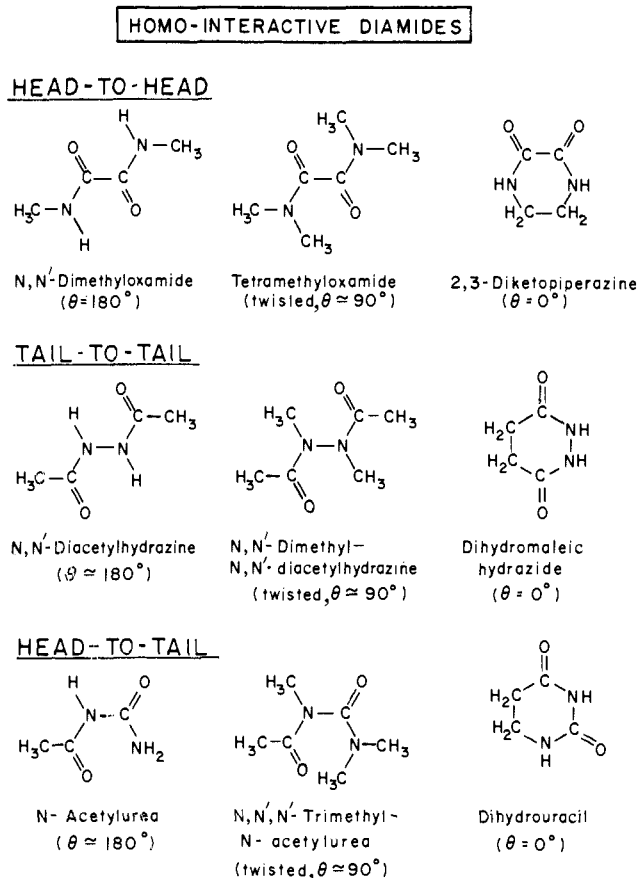


Figure 2. Molecules representative of homointeractive diamides. The dihedral angle, θ , between the two amide planes is estimated from models (see ref 4 for discussion on oxamides).

(2) **Homointeractive Diamides.** The subclass of *homointeractive* diamides can be further divided into the three categories illustrated in Figure 2. These three categories reflect the three possible bonding possibilities in the homointeractive diamides and are expected to exhibit radically different spectroscopic behavior. Furthermore, the extent of interaction for each of the three cases is expected to be very dependent on the dihedral angle, θ , between the amidic planes. This variable, if not controllable, would complicate the spectroscopy of these molecules enormously; fortunately, a proper choice of alkyl substituents can limit θ to the small range of values indicated in Figure 2.

Head-to-Head (HH) Interactions. Of the three different possibilities shown in Figure 2, only the two planar head-to-head (HH) interactions (*i.e.*, the *trans*- and *cis*-oxamides) are emissive. The emission in these instances is totally phosphorescence. The absorption and emission spectra of all three HH possibilities are shown in Figure 3B.

The electronic excited states of the oxamides are considerably lower in energy than those of the isolated amides.⁴ Relative to the corresponding isolated amide, for example, the ${}^1\Gamma_{n\pi^*}$ state of *trans*-oxamide⁴ decreases in energy¹⁵ (*i.e.*, is stabilized) by $\sim 10,000 \text{ cm}^{-1}$ whereas

(15) The term "stabilization energy" or "energy stabilization," as used here, refers to a difference of related transition energies in two different molecules. Since no knowledge of the relative energies of the two ground states exists, it follows that this datum provides no information on whether a given excited state in question is *unchanged*, *stabilized*, or *destabilized* relative to the reference molecule. Hence, the terminology has meaning only for a situation in which the ground states of the two molecules are arbitrarily taken to have the same energy. Since

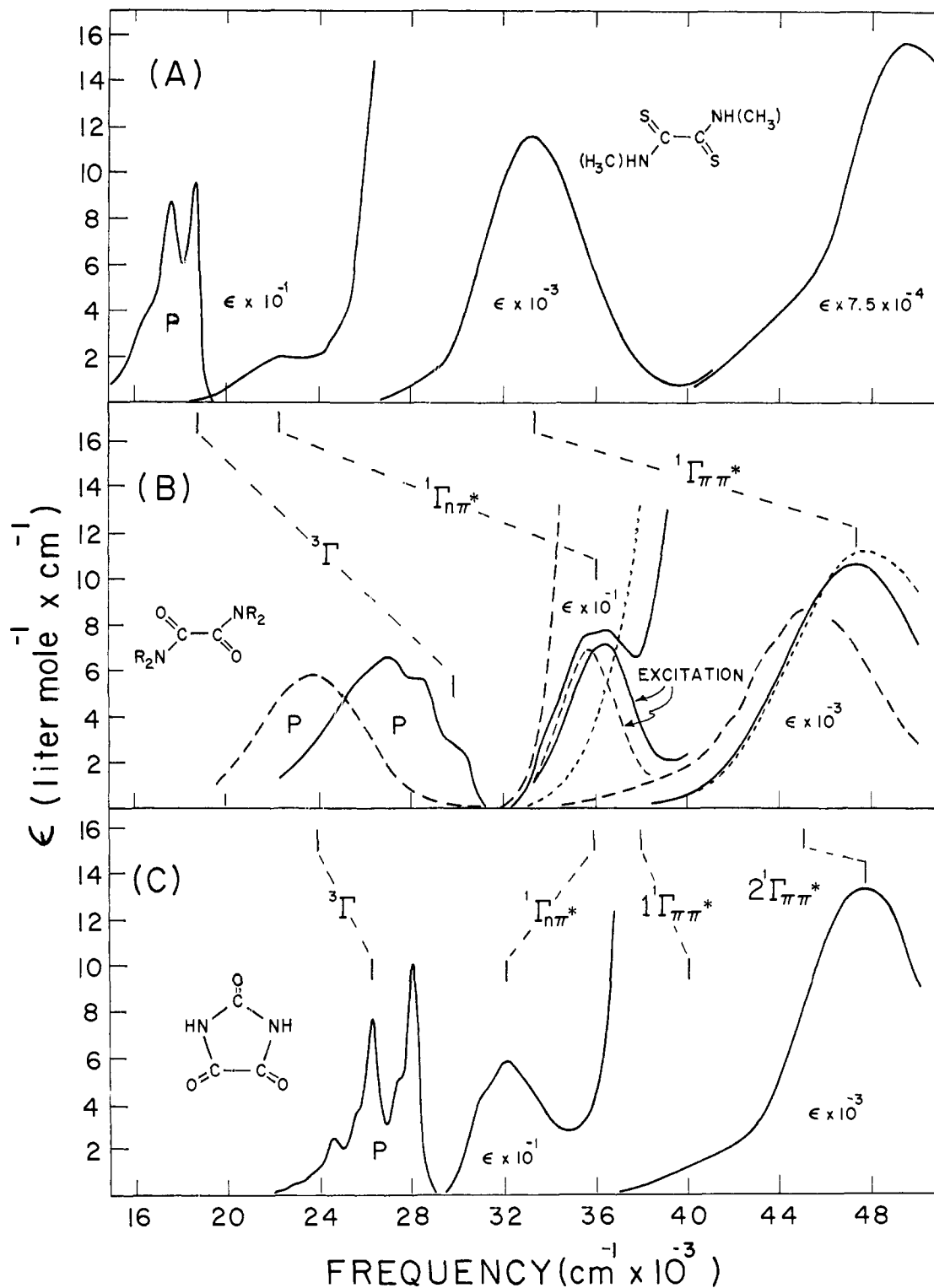


Figure 3. The luminescence and absorption spectra of (A) *N,N'*-dimethyldithioamide, (B) *trans*, *cis*, and twisted oxamides, and (C) parabanic acid. The transitions observed in these spectra are correlated and empirically labeled. The spectra of B are for *N,N'*-dipropylamide (solid line), 5,5-dimethyl-1-isopropyl-2,3-diketopiperazine (long-dash line), and tetraethylamide (short-dash line). The absorption spectra for all compounds are of acetonitrile solutions at room temperature, excepting tetraethylamide which is of a heptane solution; emission spectra are for EPA glasses at 77°K. The excitation spectra of B represent the variation of emission intensity (monitored at the emission maximum) with exciting wavelength.

the ${}^1\Gamma_{\pi\pi^*}$ state drops energetically by $\sim 6000\text{ cm}^{-1}$. For *cis*-oxamide,⁴ the corresponding stabilization

stabilization energies, as defined here, are used only to infer the relative disposition of different excited states of one molecule relative to those of a given reference molecule, this arbitrariness should cause no difficulty. The ${}^1\Gamma_{n\pi^*}$ and ${}^1\Gamma_{\pi\pi^*}$ states of amides and thioamides are very sensitive to perturbations caused by solvent and by N-methylation. Therefore,

energies¹⁵ are $\Delta({}^1\Gamma_{n\pi^*}) \simeq 10,000\text{ cm}^{-1}$ and $\Delta({}^1\Gamma_{\pi\pi^*}) \simeq 10,000\text{ cm}^{-1}$. In the case of twisted oxamide,⁴ the

relative stabilization energies for a given interactive (thio)amide/isolated (thio)amide couple must be evaluated from absorption data for similarly substituted couples in the same solvent medium. The most convenient solvent medium is water or ethanol and the stabilization energies quoted throughout this paper refer to these media.

stabilization energies are quite small and are $\Delta(^1\Gamma_{n\pi^*}) \simeq 4000 \text{ cm}^{-1}$ and $\Delta(^1\Gamma_{\pi\pi^*}) \simeq 500 \text{ cm}^{-1}$. The twisted oxamides, as stated, are nonemissive.

The phosphorescence properties of the oxamides do not allow an unambiguous characterization of the T_1 state. Indeed, identification requires recourse to a correlation⁴ of the excited state properties within the isoelectronic series of α -dicarbonyls of which *trans*-oxamide is a prominent member. Such an empirical correlation is shown in Figure 4. Apart from oxamide, all of the α -dicarbonyls listed in Figure 4 exhibit clear-cut $^3\Gamma_{n\pi^*} \rightarrow ^1\Gamma_1$ phosphorescence; the phosphorescences are intense, possess well-defined vibrational progressions in a C=O stretching frequency, possess an intense origin band, and exhibit decay times $\tau_p \simeq 10^{-3}$ sec. Relative to these characteristics, the oxamide phosphorescence is quite unique; the intensity falls in the weak-to-medium range, the spectrum is either structureless or exhibits poorly defined vibrational intervals of $\sim 1500 \text{ cm}^{-1}$, the Franck-Condon pattern is quite anomalous, and the luminescence lifetime is $\tau_p \simeq 10^{-2}$ sec. This classification disparity of the oxamide phosphorescence relative to that of other members of the α -dicarbonyl set can be rationalized on the basis of Figure 4 where it is observed that the $^1\Gamma_{\pi\pi^*} - ^1\Gamma_{n\pi^*}$ energy split is, in a relative sense, very small. Thus, based on reasonable estimates of the exchange energy⁴ for a $\Gamma_{\pi\pi^*}$ configuration, the T_1 state of oxamide is of either $^3\Gamma_{\pi\pi^*}$ or mixed $^3\Gamma_{n\pi^*}/^3\Gamma_{\pi\pi^*}$ emissive type. In this sense, the anomalous phosphorescence attributes of the oxamides are correlatable with a corresponding anomaly in the $^1\Gamma_{\pi\pi^*} - ^1\Gamma_{n\pi^*}$ splitting. In sum, we believe the T_1 state of *cis*- and *trans*-oxamide to be of mixed $^3\Gamma_{n\pi^*}/^3\Gamma_{\pi\pi^*}$ type.

Tail-to-Tail (TT) Interactions. Diacetylhydrazine exhibits two¹⁶ distinct absorption features: (i) a shoulder in the region $240 > \lambda > 250 \text{ m}\mu$ (this feature is clearly defined in the vapor where $\lambda_{\text{max}} = 210 \text{ m}\mu$); (ii) an intense band at $\lambda_{\text{max}} 187 \text{ m}\mu$ for which $\epsilon_{\text{max}} \sim 3000 \text{ l. mol}^{-1} \text{ cm}^{-1}$. (this band occurs at $179 \text{ m}\mu$ in the vapor phase). Both bands are assigned as $^1\Gamma_{\pi\pi^*} \leftarrow ^1\Gamma_1$ transitions on the basis of intensities, of their red-shift behavior on going from vapor to polar solvents, and of CNDO/s computational comparisons. Specifically, the quantum-chemical calculations¹⁷ predict a lowest energy $^1\Gamma_{\pi\pi^*}$ state which is substantially lower in energy than that of oxamide and a lowest energy $^1\Gamma_{n\pi^*}$ state which is substantially higher in energy than that of oxamide. This latter observation is certainly in accord with our inability to observe any $^1\Gamma_{n\pi^*} \rightarrow ^1\Gamma_1$ absorption feature in diacetylhydrazine. Indeed, our experimental and computational data indicate that the $^1\Gamma_{n\pi^*} \rightarrow ^1\Gamma_1$ absorption band should occur at $\lambda \sim 240 \text{ m}\mu$, where it would be submerged under the long-wavelength tail of the lowest energy $^1\Gamma_{\pi\pi^*} \leftarrow ^1\Gamma_1$ absorption band.

Relative to the corresponding isolated amide the $^1\Gamma_{\pi\pi^*}$ stabilization energy is $\Delta(^1\Gamma_{\pi\pi^*}) \simeq 8000 \text{ cm}^{-1}$ whereas $\Delta(^1\Gamma_{n\pi^*}) \leq 3000 \text{ cm}^{-1}$. Thus, the TT interactions lead to a preferential stabilization of $^1\Gamma_{\pi\pi^*}$ states. Diacetylhydrazine was found to be nonluminescent.

Head-to-Tail (HT) Interactions. Two homointeractive

(16) We attribute a third absorption feature (the weak $285\text{-m}\mu$ band) to impurity for the reasons outlined in the Experimental Section.

(17) The computations were obtained using the CNDO/s-CI program as outlined in ref 4 and 5.

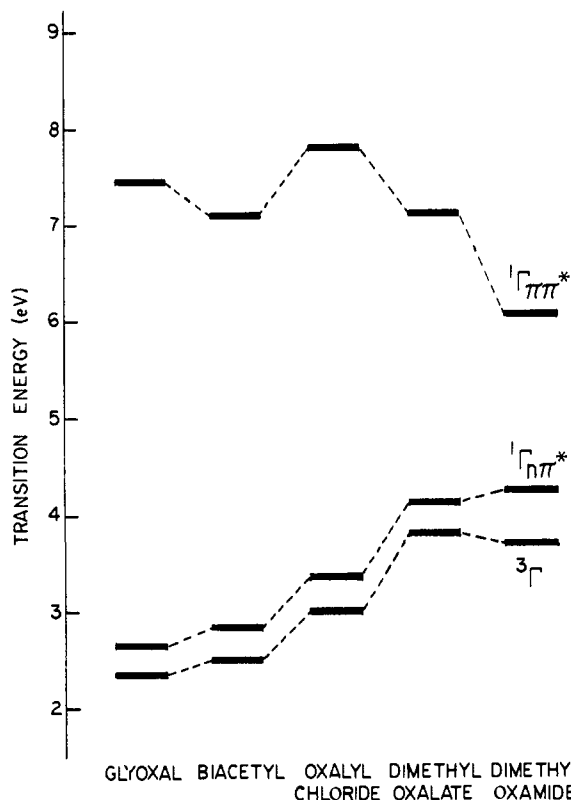


Figure 4. Correlation of transition energies of symmetric α -dicarbonyls. All $^1\Gamma_{\pi\pi^*}$ energies refer to the vapor phase and all $^3\Gamma_{n\pi^*}$ and $^3\Gamma$ energies refer to crystal, unless otherwise indicated. Data have been extracted from the following sources. Glyoxal ($^1\Gamma_{n\pi^*}$ and $^3\Gamma$ in vapor): G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, Van Nostrand, Princeton, N. J., 1967, pp 538, 539, and 635. Biacetyl: J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, **77**, 6471 (1955); V. R. Ells, *ibid.*, **60**, 1864 (1938). Oxalyl chloride ($^1\Gamma_{n\pi^*}$ and $^3\Gamma$ in vapor): W. J. Balfour and G. W. King, *J. Mol. Spectrosc.*, **25**, 130 (1968); H. Shimada, R. Shimada, and Y. Kanda, *Bull. Chem. Soc. Jap.*, **41**, 1289 (1968). Dimethyl oxalate: H. J. Maria and S. P. McGlynn, *J. Mol. Spectrosc.*, **42**, 177(1972); *ibid.*, **32**, 296(1972). Dipropylamide: ref 4.

amides, *N*-acetylurea and hydantoin, were examined in detail. A weak absorption band ($\epsilon \sim 50 \text{ l. mol}^{-1} \text{ cm}^{-1}$) is evident as a shoulder feature in the region $260 > \lambda > 230 \text{ m}\mu$ and is identified as a $^1\Gamma_{n\pi^*} \leftarrow ^1\Gamma_1$ transition. A second, more intense, absorption band is found in ethanol solutions at higher energies: at $193 \text{ m}\mu$ ($\epsilon \sim 1400 \text{ l. mol}^{-1} \text{ cm}^{-1}$) for acetylurea and at $204 \text{ m}\mu$ ($\epsilon \sim 3500 \text{ l. mol}^{-1} \text{ cm}^{-1}$) for hydantoin. In water solutions, this absorption band is still present in hydantoin at $\lambda 204 \text{ m}\mu$; however, it is now a shoulder feature to an intense band ($\epsilon_{185} > 12,000 \text{ l. mol}^{-1} \text{ cm}^{-1}$) which maximizes at $\lambda < 185 \text{ m}\mu$. These experimental data for two representative HT molecules imply¹⁸ a $^1\Gamma_{n\pi^*}$ stabilization of $\sim 2000 \text{ cm}^{-1}$ and a $^1\Gamma_{\pi\pi^*}$ energy reduction of $\sim 3500 \text{ cm}^{-1}$. All HT diamides examined were found to be nonluminescent.

(3) **Homointeractive Dithioamides.** The absorption and emission spectra⁹ of *N,N'*-dimethyldithiooxamide are given in Figure 3A. Relative to appropriate thioamides,¹⁵ the *trans*-planar dithiooxamides yield stabilization energies of $\Delta(^1\Gamma_{n\pi^*}) \simeq 9250 \text{ cm}^{-1}$ and $\Delta(^1\Gamma_{\pi\pi^*}) \simeq 5300 \text{ cm}^{-1}$. The twisted dithiooxamides,

(18) The reference-isolated amide to which the energy levels of *N*-acetylurea were compared in evaluating the quoted stabilization energies was *N*-acetyl-L-proline amide.

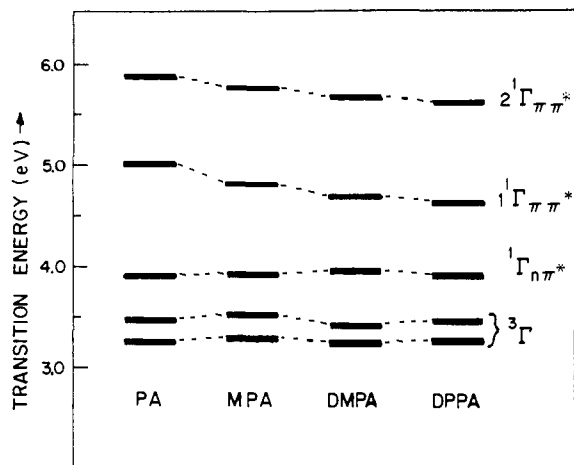


Figure 5. Correlation diagram of the experimental energies for the four lowest energy transitions of parabanic acid (PA), methylparabanic acid (MPA), dimethylparabanic acid (DMPA), and dipropylparabanic acid (DPPA). The singlet energies represent absorption maxima in water solution for $1^1\Gamma_{\pi\pi^*}$ and $2^1\Gamma_{\pi\pi^*}$ and ether solution for $1^1\Gamma_{n\pi^*}$; the energies for $3^1\Gamma$ represent the first two vibronic bands of the emissions in EPA at 77°K.

much like the twisted oxamides, experience very little stabilization; for example, $\Delta(1^1\Gamma_{\pi\pi^*}) \simeq 400 \text{ cm}^{-1}$ for tetramethyldithiooxamide. Thus, relative to the appropriate thioamides, the dithiooxamides behave in a manner virtually identical with that of the corresponding oxamide/amide couples. Furthermore, as Figures 3A and 3B indicate, the excited state energies of dithiooxamide are lower than those of oxamide by rather large amounts: $\simeq 14,000 \text{ cm}^{-1}$ (or 1.7 eV) for both the $1^1\Gamma_{n\pi^*}$ and $1^1\Gamma_{\pi\pi^*}$ states. Not surprisingly, this decrement is completely comparable to the $\sim 14,500 \text{ cm}^{-1}$ energy difference of both of the corresponding sets of states in the thioacetamide/acetamide couple.¹⁹

The trans-planar dithiooxamides, as do the oxamides, exhibit a luminescence which is solely phosphorescence. However, the emission properties contrast strikingly; the dithiooxamide emission is at much lower energies; $\Phi_p(\text{thio}) \geq 10\Phi_p(\text{oxo})$; $\tau_p(\text{thio}) \simeq 10^{-3}\tau_p(\text{oxo})$; and the Franck-Condon profiles are very dissimilar. There is no doubt⁹ that the T_1 state of the dithiooxamide is of $3^1\Gamma_{n\pi^*}$ type, that its very short lifetime is due to the internal heavy-atom spin-orbit coupling effect of the sulfur center, and that the very small $1^1\Gamma_{n\pi^*} - 3^1\Gamma_{n\pi^*}$ energy splitting of $\sim 1500 \text{ cm}^{-1}$ is the result of smaller 3p-exchange integrals on the sulfur center.

Therefore, the primary difference within the planar dithiooxamide/oxamide couple is that the mixed $3^1\Gamma_{n\pi^*}/3^1\Gamma_{\pi\pi^*}$ moderately luminescent state of the latter has been converted into a strongly luminescent $3^1\Gamma_{n\pi^*}$ state of the former.

(19) In violation of the spirit of ref 15, we will now make an attempt to relate relative stabilization energies to both ground and excited state energies. In specific, it is tempting to discuss the effects of the replacement of oxygen by sulfur on ground state energies. For the isolated thio-oxo pair, these reductions, as obtained from ionization data,²⁰ are, per Koopmans' theorem, $\Delta(n \text{ MO}) \simeq 1.3 \text{ eV}$; $\Delta(\pi_o \text{ MO}) \simeq 1.1 \text{ eV}$. For the *interactive* thio-oxo pair, the same reductions are $\Delta(n \text{ MO}) \simeq 0.9 \text{ eV}$; $\Delta(\pi_o \text{ MO}) \simeq 0.8 \text{ eV}$. Thus, the 1.7-eV drop experienced by the $1^1\Gamma_{n\pi^*}$ and $1^1\Gamma_{\pi\pi^*}$ states in all thio-oxo couples must be attributed to a complex sum of effects resulting from changes in ground state ionization potentials, in π^* MO energies, in Coulomb integrals, and in exchange integrals.

(20) From a PES study of oxamides, dithiooxamides, α -dicarbonyls, etc.: J. F. Arnett, D. B. Larson, J. Meeks, and S. P. McGlynn, to be submitted for publication.

(4) Heterointeractive Amides. Pyruvamide and ethyl oxamate²¹ serve to exemplify the class of heterointeractive amides. From the standpoint of our amidic classification scheme, pyruvamide results from the bonding of a carbonyl and an amide unit and ethyl oxamate results from the bonding of an ester and an amide.

The stabilization energies of the pyruvamide states, relative to those of amide, are considerably larger than those found for the oxamides: $\Delta(1^1\Gamma_{n\pi^*}) \simeq 19,000 \text{ cm}^{-1}$ and $\Delta(1^1\Gamma_{\pi\pi^*}) \simeq 9000 \text{ cm}^{-1}$. The strong phosphorescence exhibited by pyruvamide is typical of the α -dicarbonyl molecules of Figure 4, oxamide excepted, and is clearly of $3^1\Gamma_{n\pi^*} \rightarrow 1^1\Gamma_1$ type.

On the other hand, the interactions present in ethyl oxamate²² appear to be similar to those found for *trans*-oxamide, at least with respect to stabilization energies; the $1^1\Gamma_{n\pi^*}$ state is lowered by $\sim 10,000 \text{ cm}^{-1}$ and the $2^1\Gamma_{\pi\pi^*}$ state by $\sim 6800 \text{ cm}^{-1}$. The emissivity is certainly not of $3^1\Gamma_{n\pi^*} \rightarrow 1^1\Gamma_1$ type and, in contrast to that of *trans*-oxamide, resembles that of the isolated amides (*i.e.*, $\Phi_p \leq 10^{-4}$).

(5) Biinteractive Amides. The Parabanic Acids. The absorption and luminescence spectra of parabanic acid are shown in Figure 3C. Recent investigations⁵ confirm the utility of a composite molecule approach in which parabanic acid is viewed as a sum of *cis*-oxamide and carbonyl parts. Relative to the *cis*-oxamide parentage, the $1^1\Gamma_{n\pi^*}$ state of parabanic is slightly stabilized (see Figure 3C), whereas the two $1^1\Gamma_{\pi\pi^*}$ states are destabilized. A more definitive comparison, especially for the $1^1\Gamma_{\pi\pi^*}$ states, is impossible because of the dissimilarity of N-substitutions in the two molecules.

The lowest energy $n\pi^*$ configuration of parabanic acid is predicted⁵ to possess dominant excitation amplitude on the *cis*-oxamide portion of the molecule. This conclusion is in complete accord with the vibrational analysis of the phosphorescence spectrum where the extensive α -dicarbonyl character of the excitation becomes obvious. Thus, the effect of the carbonyl substitution on the *cis*-oxamide has been to produce a conversion of phosphorescence characteristics from those typical of a *cis*-oxamide to those which are definitive for a typical α -dicarbonyl (see the prior discussion on homointeractive diamides).

The effects of methylation on the phosphorescence characteristics of parabanic acid are instructive. A correlation diagram similar to that of Figure 4 for the α -dicarbonyls is shown in Figure 5 for the parabanic acids. It is seen that alkyl substitution leads to a preferential stabilization of the $1^1\Gamma_{\pi\pi^*}$ states in going from parabanic acid to di-*n*-propylparabanic acid. While parabanic acid and monomethylparabanic acid possess typical α -dicarbonyl phosphorescence properties, the dialkyl derivatives exhibit a reversion of phosphorescence characteristics to ones which are symptomatic of the planar oxamides. Thus, the effects of dimethylation counteract those of the monocarbonyl bridging which converts *cis*-oxamide to parabanic acid: the T_1 state of *cis*-oxamide is of $3^1\Gamma_{n\pi^*}/3^1\Gamma_{\pi\pi^*}$ type; that of parabanic acid and its monomethyl derivative is of

(21) D. B. Larson, J. F. Arnett, and S. P. McGlynn, to be submitted for publication.

(22) Oxamic acid belongs to the C_s point group. All four low-energy $1^1\Gamma_{\pi\pi^*} \leftarrow 1^1\Gamma_1$ transitions are electric-dipole allowed. Thus, like *cis* oxamide, the two lowest energy $1^1\Gamma_{\pi\pi^*} \leftarrow 1^1\Gamma_1$ states are optically detectable in the $\lambda \geq 185 \text{ m}\mu$ range.

${}^3\Gamma_{n\pi^*}$ type; and that of dimethylparabanic acid is of ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ type.

Correlation of Emission Properties

(1) **Energy and Orbital Nature of the T_1 State of an Isolated Amide.** The properties of the T_1 state of an isolated amide are not accessible to phosphorimetric techniques because such states are not emissive. As a result, we now resort to correlative devices.

The available experimental information for the excited electronic states of a planar oxamide/amide couple is sketched in Figure 6. The data shown for all ${}^1\Gamma_{\pi\pi^*}$ and ${}^1\Gamma_{n\pi^*}$ states is quite secure. The T_1 state of amide is, of course, unknown, whereas the T_1 state characteristics of oxamide are ambiguous. This ambiguity forces consideration of the two cases, I and II, diagrammed in Figure 6. The T_1 state of a planar oxamide is of mixed ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ type, with no conclusion possible concerning which of the two pure configurational types supplies the dominant contribution to the actual T_1 state. Thus, the two situations depicted represent, in the case I, a T_1 state of largely ${}^3\Gamma_{\pi\pi^*}$ character with another state of largely ${}^3\Gamma_{n\pi^*}$ character at somewhat higher energies and, in case II, the inverse situation.

Implicit in the diagram is the assumption that the ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ interaction is vibronic and that it does not lead to any massive energy perturbations. This assumption implies that the energy gap between mixing triplet states is $E \leq 2000 \text{ cm}^{-1}$, an estimate based on experimental evidence²³ available for systems of strongly mixed ${}^3\Gamma_{n\pi^*}$ and ${}^3\Gamma_{\pi\pi^*}$ states and on the expectation that efficient coupling between states is not predicted when the energy gap becomes larger than the frequencies of perturbing vibrations. It is also assumed, in both cases, that the singlet-triplet energy splittings $E({}^1\Gamma_{n\pi^*}) - E({}^3\Gamma_{n\pi^*})$ and $E({}^1\Gamma_{\pi\pi^*}) - E({}^3\Gamma_{\pi\pi^*})$ remain unchanged in proceeding from the oxamide to the amide. This latter assumption is excellent for the ${}^1\Gamma_{n\pi^*} - {}^3\Gamma_{n\pi^*}$ splitting interval in view of the highly localized nature of the excitation in such states. In the case of the ${}^1\Gamma_{\pi\pi^*} - {}^3\Gamma_{\pi\pi^*}$ splitting, a larger separation is expected in the isolated amide because of its smaller size.²⁴ Fortunately, such a larger splitting aids rather than hinders our arguments.

We now discuss cases I and II individually. Case I (${}^3\Gamma_{\pi\pi^*}$ lower): the energy of the nominal ${}^3\Gamma_{n\pi^*}$ state of oxamide is assumed to lie higher than the T_1 state by an amount $E \leq 1500 \text{ cm}^{-1}$. The upper limit for the energy gap is taken to be less than 2000 cm^{-1} so that a rather normal singlet-triplet split of $2500 \leq E_{ST} \leq 4000 \text{ cm}^{-1}$ will obtain for the ${}^1,{}^3\Gamma_{n\pi^*}$ states. If we now

(23) For example, the ${}^3\Gamma_{n\pi^*} - {}^3\Gamma_{\pi\pi^*}$ energy gap for a rigid α,β -unsaturated ketone [C. R. Jones, D. R. Kearns, and R. M. Wing, *J. Chem. Phys.*, **58**, 1370 (1973)] is $1000\text{--}2000 \text{ cm}^{-1}$ and for tetramethylpyrazine (R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, **49**, 971 (1968)] is $\sim 1900 \text{ cm}^{-1}$.

(24) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, pp 75-83. This generalization (*i.e.*, that the more delocalized the excitation, the smaller the S-T split) is based on data for cata-condensed hydrocarbons, polymethinium salts, and polyphenyls. Recent particle-impact data (which provides S_1 and T_1 energies in the same spectrum under identical experimental conditions) provide a good comparison for ethylene and butadiene. For electron impact [J. P. Doering and A. J. Williams, *J. Chem. Phys.*, **47**, 4180 (1967), and O. A. Mosher, W. M. Flicker, and A. Kuppermann, *Chem. Phys. Lett.*, **19**, 332 (1973)], $E_{ST}(\text{ethylene}) = 26600 \text{ cm}^{-1}$ and $E_{ST}(\text{butadiene}) = 21,900 \text{ cm}^{-1}$; for ion impact [J. H. Moore, Jr., *J. Phys. Chem.*, **76**, 1130 (1972)], $E_{ST}(\text{ethylene}) = 28,300 \text{ cm}^{-1}$ and $E_{ST}(\text{butadiene}) = 23,500 \text{ cm}^{-1}$.

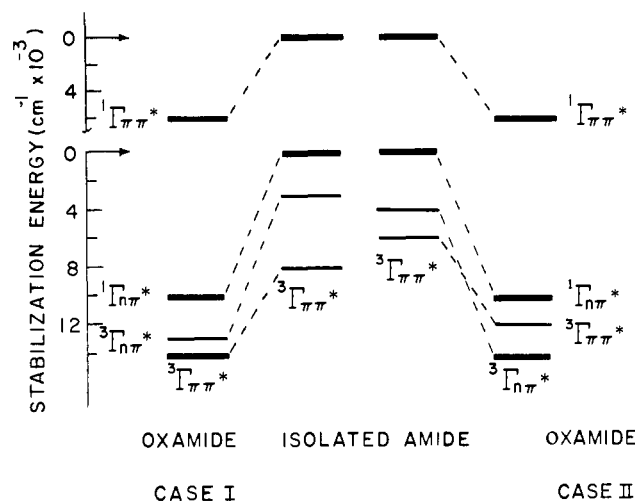


Figure 6. Correlation diagram for the oxamide/amide couple. Heavy lines indicate experimentally derived energies; light lines indicate speculative energies. Two stabilization-energy scales are shown, one relative to the ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ energy of amide and the other to the ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma$ energy. The observed E_{ST} energy of oxamide absorption and emission is plotted on the stabilization energy scale for the ${}^1\Gamma_{n\pi^*}$ state. The difference between the ${}^1\Gamma_{n\pi^*}$ and ${}^1\Gamma_{\pi\pi^*}$ states of amide is that observed for acetamide in water solution.

utilize the experimental conclusion concerning the preferential destabilization of ${}^1\Gamma_{n\pi^*}$ states, relative to ${}^1\Gamma_{\pi\pi^*}$ states, in going from oxamide to amide and if we assert a constancy of singlet-triplet splits in both the amide and oxamide, we predict that the T_1 state of an isolated amide is of ${}^3\Gamma_{\pi\pi^*}$ type and that the ${}^3\Gamma_{n\pi^*}$ state lies $\sim 5000 \text{ cm}^{-1}$ toward higher energies. Such a separation (*i.e.*, 5000 cm^{-1}) seems too large for the induction of much vibronic mixing of ${}^3\Gamma_{n\pi^*}$ and ${}^3\Gamma_{\pi\pi^*}$ states; hence, we conclude that the T_1 state of the isolated amide is of "pure" ${}^3\Gamma_{\pi\pi^*}$ type.

Case II (${}^3\Gamma_{n\pi^*}$ lower): the energy of the nominal ${}^3\Gamma_{\pi\pi^*}$ state of oxamide is assumed to lie higher than the T_1 state by an amount $E \simeq 2000 \text{ cm}^{-1}$. General singlet-triplet splitting considerations for a $\pi\pi^*$ configuration allow this ${}^3\Gamma_{\pi\pi^*}$ state to be located at considerably higher energy. However, the observation of a heavily mixed ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ character for the oxamide phosphorescence state indicates to us that the feasible energy separation is $E({}^3\Gamma_{\pi\pi^*}) - E({}^3\Gamma_{n\pi^*}) \leq 2000 \text{ cm}^{-1}$. Proceeding now as in Case I, we again conclude that the T_1 state of the isolated amide is of ${}^3\Gamma_{\pi\pi^*}$ type. If, in addition, we allow the ${}^1\Gamma_{\pi\pi^*} - {}^3\Gamma_{\pi\pi^*}$ energy splitting to be larger in the amide than in the oxamide, we conclude that the splitting $E({}^3\Gamma_{n\pi^*}) - E({}^3\Gamma_{\pi\pi^*}) \geq 2000 \text{ cm}^{-1}$ for the amide and that the $T_1({}^3\Gamma_{\pi\pi^*})$ energy of the amide is relatively free of ${}^3\Gamma_{n\pi^*}$ contamination.

It is predicted, in both cases I and II, that the lowest triplet state of the isolated amide is ${}^3\Gamma_{\pi\pi^*}$ in nature. The energy of this state is estimated as $36,000 \text{ cm}^{-1}$ (Case I) $\leq E({}^3\Gamma_{\pi\pi^*}) \leq 38,500 \text{ cm}^{-1}$ (Case II). The singlet-triplet splitting is estimated as $23,300 \text{ cm}^{-1}$ (Case I) $\geq E({}^1\Gamma_{\pi\pi^*}) - E({}^3\Gamma_{\pi\pi^*}) \geq 15,000 \text{ cm}^{-1}$ (Case II). If, as we deduce, the T_1 states of the isolated amides are nonemissive, our predictions of ${}^3\Gamma_{\pi\pi^*}$ nature for this state are fully consistent with such nonemissivity. If, on the other hand, the very weak, long-lived emissions, which certain glassy systems exhibit in the $25,000 \simeq 22,200 \text{ cm}^{-1}$ region (see Table I), are intrinsic to the isolated amides,

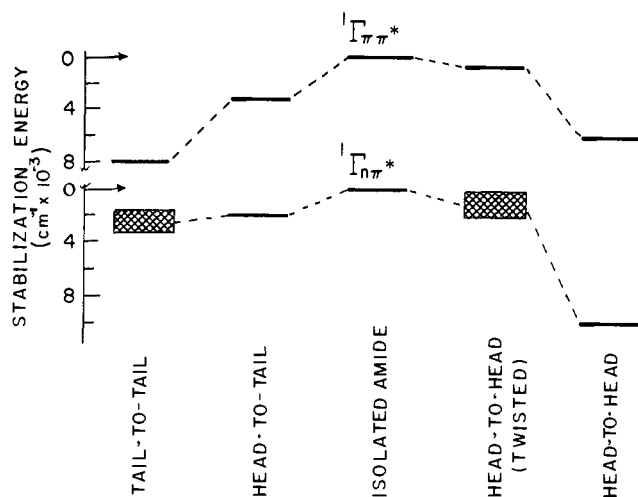


Figure 7. The ${}^1\Gamma_{\pi\pi^*}$ and ${}^1\Gamma_{n\pi^*}$ stabilization energies for homointeractive diamides relative to appropriate isolated amides. The energy scales and relative energies of the ${}^1\Gamma_{\pi\pi^*}$ and ${}^1\Gamma_{n\pi^*}$ states are those of Figure 6. The cross-hatched regions represent the energy range for expected, but unobserved, ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions. The following molecules were used to calculate stabilization energies for a given homointeractive/isolated amide couple: (i) tail-to-tail, diacetylhydrazine; (ii) head-to-tail, hydantoin, (iii) head-to-head (twisted) and head-to-head (planar), see ref 4.

then the T_1 state of isolated amides must be geometrically very different from the ground state. Certainly, it is quite difficult to conceive of a T_1 state of an isolated amide being lower in energy than that of the related oxamide. In view of this, we again conclude, in full conformity with our experimental deductions, that the observed weak emissions are not intrinsic to the isolated amides.

The conclusion that the lowest triplet state of the isolated amide is of ${}^3\Gamma_{\pi\pi^*}$ nature is in full accord with prior work.² However, the energy range estimated previously, $30,000 \geq E({}^3\Gamma_{\pi\pi^*}) \geq 22,000 \text{ cm}^{-1}$, is considerably lower than that found here, $38,500 \geq E({}^3\Gamma_{\pi\pi^*}) \geq 36,000 \text{ cm}^{-1}$. This discrepancy²⁵ is caused by the fact that the prior approach effectively "normalized" the expected T_1 energy of the CONH_2 grouping to that of the isoelectronic COOH grouping where a low-energy phosphorescence had been observed. This, it seems, might have been improper. The COOH emissions²⁶ are at very low energy and dictate a very large ${}^1\Gamma_{\pi\pi^*} - {}^3\Gamma_{\pi\pi^*}$ splitting of $\sim 40,000 \text{ cm}^{-1}$ in the COOH entity; additionally, the carboxyl group phosphorescence is also very weak and, possibly, not even intrinsic to COOH . In contrast, the conclusions presented here, based as they are on reasonable assumptions concerning the constancy of singlet-triplet splittings, appear to be quite secure.

It is also obvious that direct measurement of the T_1 state of an isolated amide is imperative. It appears to us that electron-impact spectrometry would serve this end. Considering the prior success of this method²⁷

(25) It should be noted that a radiolytic study [M. A. J. Rodgers, H. A. Sokol, and W. M. Ganison, *Biochem. Biophys. Res. Commun.*, **40**, 622 (1970)] of concentrated aqueous solutions of simple peptides, including acetylalanine, involving quenching by a series of aromatic molecules has been interpreted as evidence for a low-lying triplet state in the region $27,200 \leq E \leq 28,500 \text{ cm}^{-1}$.

(26) L. W. Johnson, H. J. Marla, and S. P. McGlynn, *J. Chem. Phys.*, **54**, 3823 (1971).

(27) A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.*, **72**, 3894 (1968); see also ref 24.

Table II. Emissivity of Amidic Molecules^{a,b}

Molecule	E_{SS} , kK	Molecule	E_{SS} , kK
(A) No emissivity ($\Phi_p \leq 10^{-4}$)			
<i>N</i> -Methylacetamide	7.3	Diacetylhydrazine	<5.0
Thioacetamide	6.2	Ethyl oxamate	9.1
Thiourea	5.6	Tetramethyloxamide	<10.6
<i>N</i> -Acetyljurea	≈ 8.5	Tetramethylthiooxamide	7.7
Hydantoin	7.3		
	E_{SS} , kK	E'_{SS} , kK	E_{ST} , kK
			τ_p , sec
(B) Weak to Intermediate Emissivity ($10^{-4} \leq \Phi_p \leq 10^{-2}$)			
<i>N,N'</i> -Dimethyloxamide	10.5		4.0
5,5-Dimethyl-1-isopropyl-2,3-diketopiperazine	3.5	9.3	5.5
Dimethylparabanic acid	5.5	14.2	3.0
Maleimide ^c	9.2	22.0	4.3
<i>N</i> -Methylmaleimide ^c	5.4	22.0	4.3
Succinimide	10.4		$\sim 10^{-3}$
(C) Intense Emissivity ($\Phi_p \geq 10^{-1}$)			
<i>N,N</i> -Dimethylthiooxamide	10.9		1.5
Parabanic acid	8.2	15.1	3.0
Pyruvamide	16.9		2.9

^a E_{SS} refers to the energy separation $E({}^1\Gamma_{\pi\pi^*}) - E({}^1\Gamma_{n\pi^*})$; when the molecule has two detectable ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ absorptions, E_{SS} refers to the difference $E({}^1\Gamma_{\pi\pi^*}) - E({}^1\Gamma_{n\pi^*})$ and E'_{SS} refers to $E({}^2\Gamma_{\pi\pi^*}) - E({}^1\Gamma_{n\pi^*})$, where $E({}^2\Gamma_{\pi\pi^*}) > E({}^1\Gamma_{\pi\pi^*})$. E_{ST} refers to the energy separation of the phosphorescence and the lowest energy ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ absorptive event. ^b All singlet energies refer to water or alcohol solutions; emission parameters refer to glassy solvents (usually EPA) at 77°K. ^c C. J. Seliskar and S. P. McGlynn, *J. Chem. Phys.*, **55**, 4337 (1971).

in detecting the T_1 states of water and butadiene, the elaboration of the ${}^3\Gamma_{n\pi^*}$ and ${}^3\Gamma_{\pi\pi^*}$ states of formamide should not be too difficult.

(2) **Orbital Nature of T_1 States of Amidic Molecules.** Having provided state assignments for amides and oxamides, a rationalization of amidic emissive properties is now possible. Of basic importance in Figure 6 is the fact that the transition from an isolated amide to a planar oxamide (HH bonding) provides for an interaction (*i.e.*, stabilization energy) which is larger for ${}^1\Gamma_{n\pi^*}$ states than for ${}^1\Gamma_{\pi\pi^*}$ states; this situation produces a decrease in the energy gap between $n\pi^*$ and $\pi\pi^*$ triplets and an increase in the energy gap between singlets. The latter energy separation is investigated further for selected homointeractive amides in Figure 7 using stabilization energies computed for appropriate diamide/isolated amide couples. A minimal stabilization energy of both ${}^1\Gamma_{n\pi^*}$ and ${}^1\Gamma_{\pi\pi^*}$ states is found for the twisted HH case. For the other bonding situations, the ${}^1\Gamma_{n\pi^*}$ state is minimally stabilized except for the HH case, while the ${}^1\Gamma_{\pi\pi^*}$ stabilization is substantial, being greatest for TT bonding.

The TT and HT bonding situations exhibit a preferential ${}^1\Gamma_{\pi\pi^*}$ stabilization, while the HH bonding gives rise to a preferential ${}^1\Gamma_{n\pi^*}$ stabilization. The resultant ${}^1\Gamma_{\pi\pi^*} - {}^1\Gamma_{n\pi^*}$ energy separation in all cases is less than or equal to that for the isolated amide except for the HH (oxamide) interaction. If one accepts the attitudes represented by Figure 6, a prediction of a lowest ${}^3\Gamma_{\pi\pi^*}$ state for *all* homointeractive amides, except the planar HH molecules, is obtained. Significantly all molecules of Figure 7 are nonemissive except for the latter type, an observation which implies that, in general, amidic ${}^3\Gamma_{\pi\pi^*}$ states are nonemissive.

Instead of using stabilization energies, the energy separation between absorptive ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ and ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transitions may be used directly to provide an indication of the emissive properties of an amidic molecule. This idea is examined in detail in Table II, where molecules are classified in terms of their phosphorescence ability. For those molecules which possess only one low-lying ${}^1\Gamma_{\pi\pi^*}$ state, a correlation between emissivity and E_{SS} is apparent: (i) if $E_{SS} < 9.0$ kK, molecules are nonemissive, (ii) if $E_{SS} \simeq 9\text{--}10.5$ kK, molecules are weakly emissive, and (iii) if $E_{SS} > 10.5$ kK molecules are strongly emissive. For those amidic molecules which possess two low-lying ${}^1\Gamma_{\pi\pi^*}$ states (e.g., *cis*-oxamides, parabanic acids and maleimides), the observed correlation is:²⁸ (iv) if $E_{SS} < 6$ kK, compounds are weakly emissive, and (v) if $E_{SS} > 7$ kK, compounds have intermediate to intense emissions. In general, Table II indicates that the larger E_{SS} the better the possibilities for an emissive T_1 state of either mixed ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ or pure ${}^3\Gamma_{n\pi^*}$ type.

Another useful parameter in Table II, but one on which information is available only for luminescent molecules, is the energy separation of the emissive triplet from the lowest ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition, E_{ST} . It is clear from Table II that a value of $E_{ST} \leq 3000$ cm^{-1} implies intense luminescence, whereas values of $3000 \leq E_{ST} \leq 5500$ cm^{-1} usually characterize the moderately intense emitters. Values of $E_{ST} > 6000$ cm^{-1} apparently dictate a weak or absent luminescence capacity.

Finally, the categorization of the molecules of Table II, according to their emission characteristics, coincides with the description of the orbital excitation nature of T_1 states already proposed (see Results, sections 1 through 5). In fact, the following generalizations concerning the T_1 states of amidic molecules may now be made: amidic T_1 states of ${}^3\Gamma_{\pi\pi^*}$ type are nonemissive (i.e., $\Phi_p \leq 10^{-4}$); amidic T_1 states of mixed ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ type exhibit weak to intermediate emissive intensity ($10^{-4} \leq \Phi_p \leq 10^{-2}$), an observed decay time of $\tau_p \simeq 10^{-2}$ sec, and E_{ST} values of 3000–5500 cm^{-1} ; amidic T_1 states of ${}^3\Gamma_{n\pi^*}$ type are intense emitters ($\Phi_p > 10^{-1}$), have observed decay times of $\tau_p \simeq 10^{-3}$ sec, exhibit prominent C=O stretching vibrational activity, and have values of $E_{ST} \leq 3000$ cm^{-1} ; the value of E_{SS} for an amidic molecule is a useful gauge of the emissive behavior of amidic T_1 states.

Table IIB contains some biinteractive molecules which have not yet been discussed: maleimide, *N*-methylmaleimide, and succinimide. The emissions of maleimide and its monoalkyl derivative have been assigned previously²⁹ as ${}^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$. However, in the case of maleimide, one must note some discrepancies relative to this assignment: the phosphorescence lifetime is 10^{-2} sec, the phosphorescence intensity lies in the weak to moderate range, and a carbonyl stretching activity is not obvious in the emission; indeed, the

(28) The two sets of criteria (i, ii, iii) and (iv, v) pertain to two different sets of ${}^1, {}^3\Gamma_{\pi\pi^*}$ states. Hence, the change of the energy splitting requirements in the set (iv, v) is not surprising. The interpretation of this observed decrease, however, is another matter. It appears that we must assume the $E({}^1\Gamma_{\pi\pi^*}) - E({}^3\Gamma_{\pi\pi^*})$ splitting to be considerably smaller for the $1\Gamma_{\pi\pi^*}$ configuration than for the $2\Gamma_{\pi\pi^*}$ configuration. (For notation, see footnote a of Table II.) If this be the case, it follows that E_{SS} has to be smaller in order for effective mixing of ${}^3\Gamma_{n\pi^*}$ and ${}^3\Gamma_{\pi\pi^*}$ to occur.

(29) C. J. Seliskar and S. P. McGlynn, *J. Chem. Phys.*, **55**, 4327 (1971).

prominent vibronic activity occurs in a 1500- cm^{-1} interval. If one couples these observations with the concomitant reductions of emission intensity and E_{SS} which occur upon *N*-methylation (i.e., preferential ${}^1\Gamma_{\pi\pi^*}$ stabilization), it would appear that the T_1 states of maleimide and *N*-methylmaleimide are best assigned as ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$. Thus, the T_1 state of *N*-methylmaleimide may be supposed to possess more ${}^3\Gamma_{\pi\pi^*}$ character than that of maleimide; indeed, one might conjecture that a nominal ${}^3\Gamma_{n\pi^*}$ state is the T_1 state of maleimide, whereas a nominal ${}^3\Gamma_{\pi\pi^*}$ state is the T_1 state of the methylated derivative. The removal of the C=C double bond of maleimide yields succinimide (see Figure 1) and, as seen in Table II, this increases the E_{SS} value by ~ 1000 cm^{-1} , reduces the luminescence decay time to $\sim 10^{-3}$ sec, but leaves the intermediate emission intensity unaltered at a level comparable to that of maleimide. In line with our previous attitudes, we view the preferential ${}^1\Gamma_{\pi\pi^*}$ destabilization which occurs upon removal of the double bond as leading to a greater degree of ${}^3\Gamma_{n\pi^*}$ character in the T_1 state of succinimide.

(3) **Correlation of Absorption and Emission Properties of Amidic Molecules.** The ideas developed in sections 1 and 2 may now be used to provide general correlation of the spectroscopic properties of amidic molecules. Figure 8 shows the results obtained using selected examples of all the types of amidic molecules classified in Figure 1.

The energy diagram of Figure 8 is basically an extension of Figure 6 except that observed transition energies are used instead of relative stabilization energies. The two cross-hatched areas for *N*-methylacetamide represent the energy ranges deduced from consideration of Cases I and II of Figure 6. In addition, the energy of a low-lying, experimentally unobserved, and theoretically forbidden ${}^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ transition, as computed by CNDO/s-CI techniques, is included for dimethylloxamide; its correlation to a state of *cis*-oxamide is made on the basis of CNDO/s-MO correlations.⁴ The correlations for the ${}^1\Gamma_{\pi\pi^*}$ energies for *cis*-oxamide and the parabanic acids, as well as for ethyl oxamate and pyruvamide, are made on the basis of transition intensity comparisons and CNDO/s-CI computations.¹⁷ The ${}^1\Gamma_{n\pi^*}$ correlation is based on experimental data which indicate that the lowest energy absorptive transition is identical for all these molecules.^{4,5,21} The lowest triplet state designations of Figure 8 are those we have previously discussed.

For the most part, the triplet energies given in Figure 8 represent experimental energies obtained from emission data. The range of energies shown for the isolated amide is given earlier in association with Figure 6. For the other nonemissive molecule, ethyl oxamate, the estimate of the energy of the proposed lower lying ${}^3\Gamma_{\pi\pi^*}$ state is based on an energy estimate for the ${}^3\Gamma_{n\pi^*}$ state; an empirical generalization of α -dicarbonyl emissive energies indicates that the emission of a mixed α -dicarbonyl always falls intermediate to the emission energies of the two symmetric (or "pure") α -dicarbonyls to which it is related. Thus, the ${}^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ emissions of oxamides and oxalic acid place the similar transition energy of ethyl oxamate in the narrow energy range 29.4–30.8 kK. The nonemissivity of ethyl oxamate, as per earlier generalizations, then puts the ${}^3\Gamma_{\pi\pi^*}$ state well below the ${}^3\Gamma_{n\pi^*}$ state. On the other hand, the

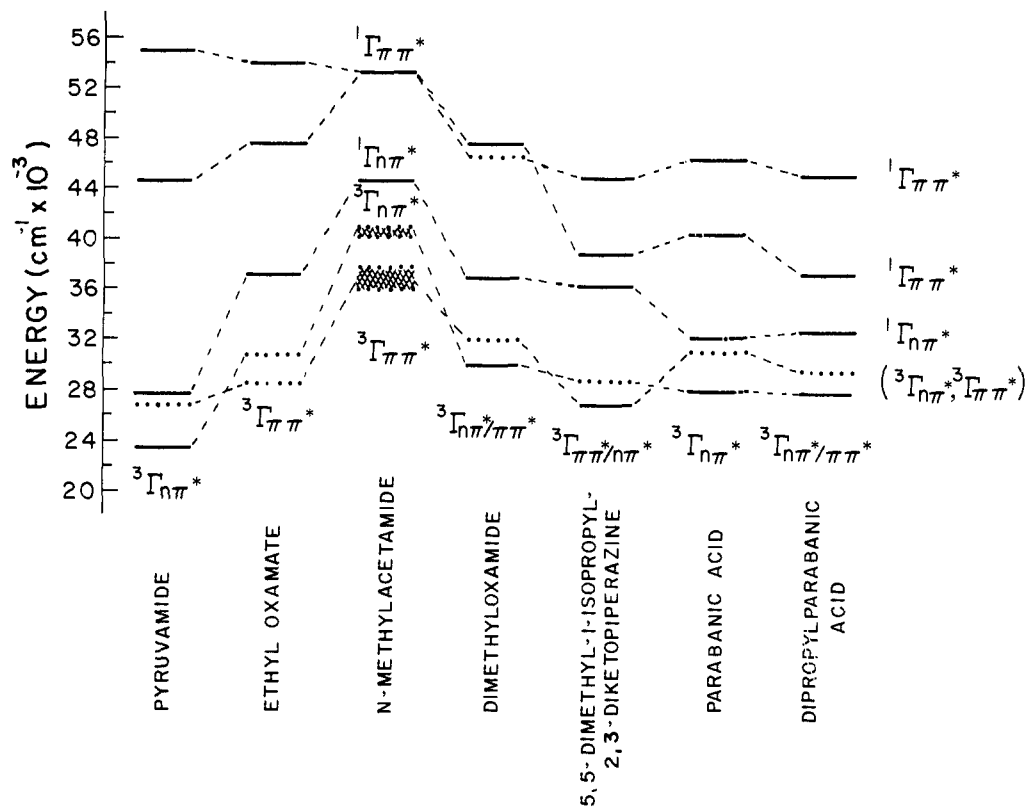


Figure 8. Correlation diagram for the lower energy excited states of a number of amidic molecules. Solid lines are the observed transition energies from absorption or emission spectra and dotted lines are transition energies inferred by some correlative or theoretical technique; the cross-hatched regions for acetamide represent the energy ranges of ${}^3\Gamma_{n\pi^*}$ and ${}^3\Gamma_{\pi\pi^*}$ predicted from Figure 6. See text for discussion of triplet state assignments and correlations.

undoubted ${}^3\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ emission of pyruvamide surely places its ${}^3\Gamma_{\pi\pi^*}$ state several kK to higher energies. The location of the ${}^3\Gamma_{n\pi^*}$ state of pyruvamide is retained below that of the ${}^1\Gamma_{n\pi^*}$ state so as to afford efficient intersystem emitting to the triplet manifold. The energy of the nominal ${}^3\Gamma_{n\pi^*}$ state of the molecules which exhibit mixed ${}^3\Gamma_{n\pi^*}/{}^3\Gamma_{\pi\pi^*}$ emissions is based on the premise that the two states must lie within ~ 2000 cm^{-1} of each other for substantial mixing. The positioning of the ${}^3\Gamma_{\pi\pi^*}$ state in parabanic acid is based on reasoning similar to that used for pyruvamide.

Thus, based on experimental absorption and emission energies and the generalizations given previously, one is able to rationalize the diverse emissive properties of these molecules, to give T_1 state assignments, to provide energy estimates of the T_1 state for nonemissive

molecules, and even to deduce T_2 state assignments and energy estimates.

Consequences Related to the Peptide Linkage

This work places the T_1 state of the peptide bond at considerably higher energies (due account being taken of ${}^1,{}^3\Gamma_{\pi\pi^*}$ stabilization of the amide states in the protein structure) than those³⁰ of such entities as phenylalanine ($T_1 \simeq 29$ kK), tyrosine ($T_1 \simeq 27$ kK), and tryptophan ($T_1 \simeq 25$ kK). It would appear then that the peptide linkage is not part of the electronic-energy transfer system of proteins. Nonetheless, given the peptide bond properties of nonemissivity and pervasiveness in the protein and enzyme primary structure, it is not unlikely that it plays a protective role.

(30) The estimates of 0,0 T_1 energies quoted here are taken from M. E. McCarville and S. P. McGlynn, *Photochem. Photobiol.*, **10**, 171 (1969).