trans host. Since the transitions of the cis and trans conformations share no common state, the energy of the cis relative to the trans form cannot be determined from the data.

Long-lived phosphorescence of the ^3A_u state of trans-biacetyl has been observed and analyzed; emission previously assigned[3] to this state is due mainly to impurities. Biacetyl is photosensitive, and the "strong green" impurity emission is easily restored by irradiation as the dominant luminescence system. Curves reported for biacetyl emission, in hydrocarbon glasses at low temperatures are remarkably similar to the "strong green" emission of the impure crystal and have

the same profile as that illustrated in Figure 2c. This profile appears in, for example, the (nonexponential) emission of biacetyl in 3-methylpentane at 1.2°K, measured by Chan and Clarke,[17] and the interpretation of this microwave-optical double resonance experiment should possibly be reconsidered.

Excited Electronic States of the α-Dicarbonyls

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Abstract: Emission and absorption spectra are presented for two α-dicarbonyls: an indanedione and a propanedione derivative. Pes spectra are also reported for the indanedione and benzil, and a circular dichroism spectrum of an indanedione is given. These data are used to describe the dependence of excited state energies on the CO/CO dihedral angle, θ. This dependence, in conjunction with CNDO/s computations on glyoxal of variable θ, provides an assignment of the two low-energy $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ excitations, in order of increasing energy, as $^1\Gamma_{n_+\pi_+^*} \leftarrow {}^1\Gamma_1$ and $^1\Gamma_{n_-\pi_+^*}/{}^1\Gamma_{n_+\pi_-^*} \leftarrow {}^1\Gamma_1$. These assignments are not in accord with those which are generally accepted.

The low-energy absorption properties of α-diketones have generally been rationalized in terms of a simple composite molecule approximation.[1] Thus the π, n, and π^* orbitals of the dicarbonyl system are generated by the interaction of the appropriate orbitals of the carbonyl subunits to produce bonding (+) and antibonding (−) combinations with the resultant ordering (in terms of decreasing binding energy) of π_+, π_-, n_+, n_-, π_+^*, and π_-^*. Moreover, the energy separation between the highest filled MO's (i.e., n_+ and n_-) has been supposed to be rather small, ~ 1000 cm^{-1} in a synperiplanar conformation and ~ 100 cm^{-1} in an antiperiplanar conformation. Coupling these considerations with the consequences of orbital overlap, the dependence of the orbital energies upon the intercarbonyl dihedral angle, θ, is seen to be that of Figure 1. Since only the $\pi_+^* \leftarrow n_+$ and $\pi_-^* \leftarrow n_-$ configuration excitations are electric-dipole allowed, it has been usual to associate the two observed low-energy $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ absorption bands of α-dicarbonyls with these excitations.

Recently, theoretical[2] and experimental[3] results have invalidated both the assumption of near degeneracy of the $n_\pm$ pair and the orbital ordering embodied in Figure 1. In particular, the $n_\pm$ orbital pair splitting is now known to be of the order of 2 eV (16,000 cm^{-1}),

with n_- being of *higher* binding energy than n_+. Consequently, all electronic spectroscopic interpretations based on Figure 1 require further consideration. The major point of the present work, then, is the provision of an alternative set of assignments. In specific, we believe that the $\pi_-^* \leftarrow n_-$ assignment for the second $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ absorption band is incorrect and that the proper assignment is $\pi_\mp^* \leftarrow n_\pm$.

Toward this end, we have investigated the electronic spectroscopy of a synperiplanar ($\theta = 0°$) α-diketone, 3,3-dimethylindanedione (I), and a twisted ($70 < \theta < 110°$) α-diketone, 1-phenyl-1,2-propanedione (II). We accept the available data[4] for an antiperiplanar ($\theta = 180°$) dialdehyde, glyoxal (III), as being representative of a transoidal dicarbonyl system. Since we have good experimental reasons to believe that the two $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions have their excitation density almost wholly localized on the α-dicarbonyl groups,[5] we feel free to develop a computational model based on the CNDO/s–CI approximational scheme for a glyoxal molecule of variable θ and to compare the results of such computations with the experimental data which are available for the three molecules mentioned.

Our experimental investigations also lead us to some conclusions concerning the assignment of higher energy electronic states; provide some information on photorotamerism in the S_1 and T_1 states of α-dicarbonyls; elaborate a novel blue-shift effect of cooling on the

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

(2) (a) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971); (b) J. R. Swensen and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

(3) (a) D. O. Cowan, R. Gleiter, J. A. Harkmall, E. Heilbronner, and V. Harnuny, *Angew. Chem., Int. Ed. Engl.*, **10**, 401 (1971); (b) see also Table III of this text.

(4) G. N. Currie and D. A. Ramsay, *Can. J. Phys.*, **49**, 317 (1971), and references therein.

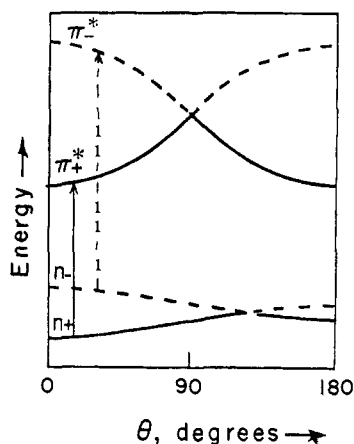(5) J. F. Arnett and S. P. McGlynn, *J. Amer. Chem. Soc.*, submitted for publication.

Figure 1. Orbital energies of an α-dicarbonyl system derived on the basis of a simple composite molecule description. The inter-carbonyl dihedral angle, θ, is defined in Figure 2. The two allowed transitions for the synperiplanar case are also shown.
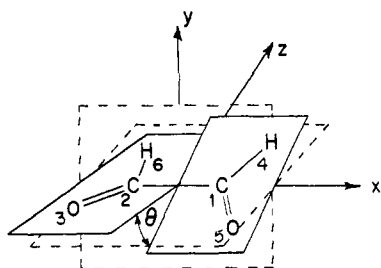

Figure 2. Atom numbering conventions, axes designations in the C_{2v} point group (i.e., synperiplanar glyoxal, θ = 0°), and the CO/CO dihedral angle for a twisted glyoxal.

phosphorescence, excitation, and absorption spectra of α-dicarbonyls and suggest that this blue-shift is dependent on effects which produce a variation of θ; indicate that twisting processes are coupled to $S_1 \rightsquigarrow S_0$ and $T_1 \rightsquigarrow S_0$ energy-dissipative channels; and, to some degree, validate a $S_1 \leftarrow T_1$ thermally activated nature for much of the room-temperature fluorescence intensity. These considerations are touched on only in the Results section since they are not particularly pertinent to our central thesis.

Experimental Section

Benzil (IV) (Baker) was purified immediately prior to use by sublimation, recrystallization, and/or thin layer chromatography. 1-Phenyl-1,2-propanedione (II) (Eastman) was subjected to multiple vacuum distillations prior to use. 3,3-Dimethylindanedione (I) was prepared by standard procedures[5] and purified as above for IV. 3-Ethyl-3-methylindanedione (V) was synthesized[6] from a (−)-phenylvaleric acid of ∼80% optical purity. The purification of camphorquinone (VI) is described elsewhere.[5]

Circular dichroism was measured using a Durrum-Jasco J-20 recording spectropolarimeter. The molar ellipticities quoted are based on a calibration of $[\theta]_{290.5}$ = 7260 deg cm²/dmol for d-10-camphorsulfonic acid in water. All other experimental techniques used have been described previously.[7]

Molecular orbital, configuration, and state energies were computed using the Del Bene–Jaffé CNDO/s-CI quantum-chemical scheme.[8] The CNDO/s program used was obtained from the Quantum Chemistry Program Exchange (QCPE 174) and was modi-

(6) R. K. Hill and G. R. Newkome, *Tetrahedron*, **25**, 1249 (1969).

(7) (a) D. B. Larson and S. P. McGlynn, *J. Mol. Spectroc.*, **47**, 469 (1973); (b) O. S. Khalil, J. L. Meeks, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **95**, 5876 (1973).

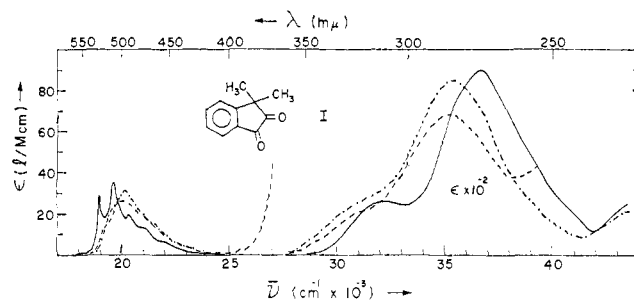(8) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

Figure 3. Absorption spectra of 3,3-dimethylindanedione (I) in solution at 300°K: (—) 3-methylpentane (3-MP) solvent, (- - -) ethanol solvent, (- ·—) acetonitrile solvent.
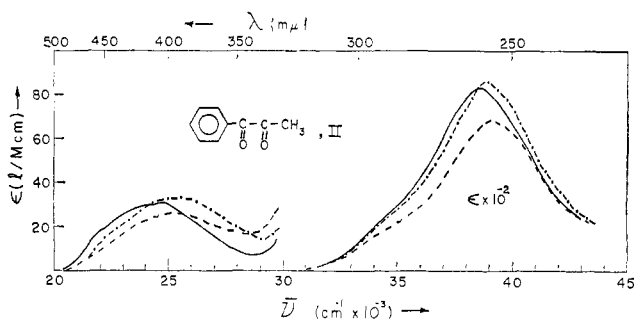

Figure 4. Absorption spectra of 1-phenyl-1,2-propanedione (II) in solution at 300°K: (−) 3-methylpentane (3-MP) solvent, (- - -) ethanol solvent, (- ·—) acetonitrile solvent.

fied to provide variable convergence criteria in the iterative procedure. Atom numbering, axes conventions in the C_{2v} point group (i.e., θ = 0°), and the CO/CO dihedral angle, θ, are defined in Figure 2. The distance matrix in the C_{2v} synperiplanar conformation, is in Chart I. Geometry is taken from data of Kuchitsu,

Chart I

Atom	Coordinate		
	x	y	z
1	0.76	0	0
2	−0.76	0	0
3	−1.38	0	−1.034
4	1.18	0	1.032
5	1.38	0	−1.034
6	−1.18	0	1.032

et al.,[9] for antiperiplanar glyoxal, and bond distances are retained invariant for all values of θ used (i.e., θ = 0, 90, and 180°). The basis set consisted of 18 AO's: 1s on H and 2s, $2p_z$, $2p_y$, and $2p_z$ on C and O. The basis set of configurations used in the configuration interaction calculations consisted of the 30 lowest energy configurations, all doubly excited configurations being excluded. In this work, we present results only for those MO's, configurations, and states which are particularly relevant to our discussion of the low-energy excited $^1\Gamma_{n\pi^*}$ states of α-dicarbonyl molecules.

Results

Absorption Studies. The absorption spectra of I and II, as obtained in various solvent media, are shown in Figures 3 and 4, respectively. These spectra are characterized by two distinct absorption regions, the lowest energy band being of weak intensity and the higher energy region, which contains two or more transitions, being of moderate-to-high intensity.

The low-energy absorption band of I in a 3-methylpentane solvent exhibits vibrational structure. This

(9) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).

Table I. Vibronic Analysis of the Lowest Energy $^1\Gamma_{n\pi}* \leftarrow {}^1\Gamma_1$ Absorption Bands of the Indanediones, I and V

λ, mμ		$[\theta]_\lambda$ (molar ellipticity)[a]	$\bar{\nu}$, cm^{-1} (absorption)	$\Delta\bar{\nu}$, cm^{-1}	Assignment ν_1, ν_2
Absorption	Circular dichroism				
528	528	163	18,940	0	0 0, 0
510	512	117	19,610	670	1, 0
490	490	58	20,410	1470	0, 1
475			21,050	1440	1, 1
458	460	14	21,830	1420	0, 2

$\nu_1 = 670$ cm^{-1}
$\nu_2 = 1440$ cm^{-1}

[a] Deg cm^2/dmol. The values of $[\theta]_\lambda$ quoted are to be considered as minimal values since they were computed assuming 100% optical purity. The actual optical purity is less than 100% (see Experimental Section).

structure is analyzed in Table I, where it is also compared with that present in the circular dichroism (CD) spectrum of V. The low-energy band of the circular dichroism spectrum of V is shown in Figure 5 and is clearly identical with the low-energy absorption band of I in 3-methylpentane shown in Figure 3. The active vibrations probably correspond to a totally symmetric carbonyl stretch ($\sim$1440 cm^{-1}) and an out-of-plane, nontotally symmetric, carbonyl bending mode ($\sim$670 cm^{-1}). The absorption band shifts to higher energy and the vibrational structure become increasingly blurred as the polarity of the solvent medium is increased.

The low-energy absorption band of II is unresolved in all media. As with I, this band blue-shifts upon progressing to solvents of higher polarity. In contrast to I, where the half-width is $\sim$1500 cm^{-1}, this band is very broad in II and exhibits a half-width of $\sim$4500 cm^{-1}. This large half-width in II is undoubtedly associated with the large range of CO/CO dihedral angles sampled in an ensemble of propanedione molecules. Indeed, the barely discernible vibronic structure found on the long-wavelength side of this absorption band in the propanedione indicates that some small fraction of the total sample exists in an antiperiplanar geometry.

The higher energy, higher extinction absorption regions are remarkably similar in both molecules. These, presumably, are transitions of $^1\Gamma_{\pi\pi} \leftarrow {}^1\Gamma_1$ type. These regions of I exhibit distinct red shifts with increasing solvent polarity, whereas those of II remain unchanged (i.e., the second band) or possibly even undergo a small blue shift (i.e., the third band). Transitions present at $\sim$300 mμ ($[\theta]_{302} = 270$) and 272 mμ ($[\theta]_{272} = -300$) in the circular dichroism spectrum of V are the counterparts of the two transitions of higher energy observed in the absorption spectrum.

On the basis of intensity considerations and solvent-shift behavior, the absorption bands of I may be assigned, in order of increasing energy, as $^1\Gamma_{n\pi}* \leftarrow {}^1\Gamma_1$, $^1\Gamma_{\pi\pi}* \leftarrow {}^1\Gamma_1$ (or $^1\Gamma_{n\sigma}* \leftarrow {}^1\Gamma_1$), and $^1\Gamma_{\pi\pi}* \leftarrow {}^1\Gamma_1$. By analogy, similar assignments hold for II. The geometry of I is planar (or nearly planar) synperiplanar; that of II is dominantly in the CO/CO dihedral angle range $70 < \theta < 110°$, with a small fraction feasible even at $\theta \simeq 180°$. This geometric motility of II is held responsible for the large band width of the $^1\Gamma_{n\pi}* \leftarrow {}^1\Gamma_1$ process, for the red-edge structure found in this same
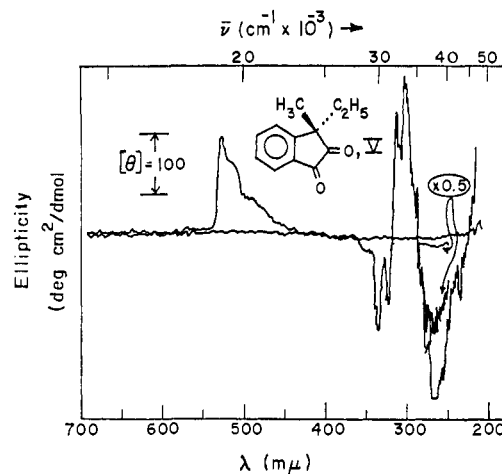

Figure 5. Circular dichroism spectrum of 3-ethyl-3-methylindanedione (V) in methylcyclohexane at 300°K. The horizontal lines are base lines. The optical purity of this sample is less than 80%.

band, and for the nondiscriminatory nature of solvent polarity effects on the second and third absorption regions.[5, 10]

The CD spectra of V in a methylcyclohexane solvent are shown in Figure 5. The low-energy band of this spectrum is compared with that of I in Table I; both bands are clearly identical. The molar ellipticities quoted in Table I refer to an optically pure sample; however, since the starting enantiomorph was only 80% purity, the actual optical purity of V is really unknown.

A second structured band is observed in the CD spectrum of 3-ethyl-3-methylindanedione at $\sim$350 mμ ($[\theta]_{335} \simeq -157$). This band possesses three well-defined vibrational peaks spaced by 1240 cm^{-1}, which we take to be a symmetric, carbonyl stretching frequency considerably reduced from that in the ground state. This band has no counterpart in the absorption spectrum. We assume that it represents a second $^1\Gamma_{n\pi}* \leftarrow {}^1\Gamma_1$ transition which is occluded beneath the long-wavelength tail of the second absorption band and which, as a result, is not detected in absorption. This conclusion is fully supported by the presence of an analogous band in the absorption spectrum of 3,3,5,5-tetramethylcyclopentanedione (VII)[11] with a vibrational spacing of $\sim$1300 cm^{-1} as well as by investigations of Charney and Tsai[12] on VI.

Emission Studies. The luminescence spectra of I and II are shown in Figures 6 and 7, respectively, where they are contrasted with the $^1\Gamma_{n\pi}* \leftarrow {}^1\Gamma_1$ absorption bands. Pertinent data are summarized in Table II. Fluorescence is observed at 300°K but not at 77°K. The distinction between fluorescence and phosphorescence at room temperature is made using a quenching technique based on simple aeration.[5] Aeration of a thoroughly degassed solution diminishes the phosphorescence considerably while leaving the fluorescence intensity essentially unaltered.

Two vibrational modes are coupled to the fluorescence and phosphorescence of I: a 1070-cm^{-1} interval

(10) J. F. Arnett, D. B. Larson, and S. P. McGlynn, *J. Amer. Chem. Soc.*, **95**, 7599 (1973).

(11) C. Sandris and G. Ourisson, *Bull. Chim. Soc. Fr.*, **23**, 958 (1956).

(12) E. Charney and L. Tsai, *J. Amer. Chem. Soc.*, **93**, 7123 (1971).

Table II. Effects of Temperature on Band Maxima of Fluorescence, Phosphorescence, Phosphorescence Excitation, and Absorption Spectra[a]

Compd	Solvent[b]	T, °K	λ(A), mμ	λ(F), mμ	λ(P), mμ	λ(EXC), mμ	τ_p, msec
I	EP	300	525, 507	529, 552	590		
I	3-MP	300	529, 510	531, 552	592		
I	EP	77	511, 494		578		5.70
I	3-MP	77			586.5		2.51
II	EP	300	(456), 404	484	541	460, 420	
II	3-MP	300	(460), 404	483.5	541	460, 420	
II	EP	77	406		530	430	3.28
II	3-MP	77			538	435	2.02

[a] A in λ(A) denotes absorption; F denotes fluorescence; P denotes phosphorescence; and EXC denotes phosphorescence excitation.
[b] EP denotes a 1:1 (v/v) mixture of ether and isopentane; MCH denotes methylcyclohexane.
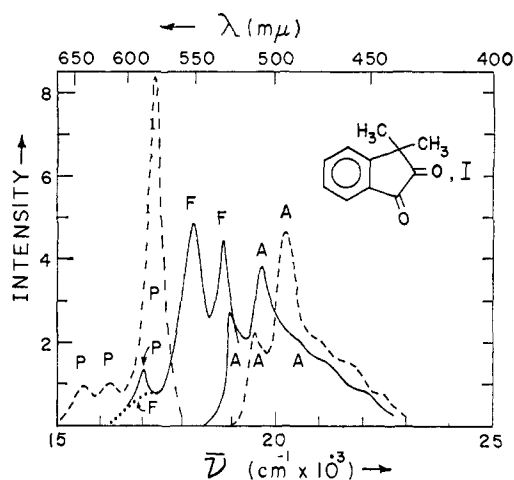

Figure 6. Absorption and emission spectra of 3,3-dimethylindane-dione (I) in ether/isopentane mixed solvent. (—) Spectrum at 300°K in a degassed fluid solvent. The dotted portion of the emission spectrum illustrates the effects of aeration and discriminates the readily quenched phosphorescence from the fluorescence. Where no dotting is shown, the solid line and the dotted line are coincident. (- - -) Spectrum at 77°K in a degassed, glassy system. Absorption, fluorescence, and phosphorescence peaks are discriminated, where necessary, by letters A, F, and P, respectively.
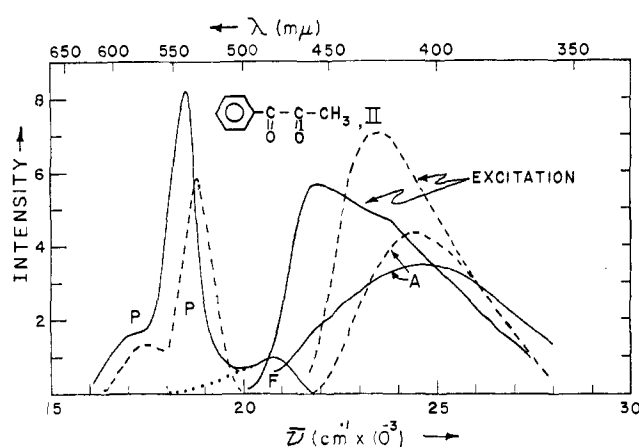

Figure 7. Absorption, emission, and emission excitation spectra of 1-phenyl-1,2-propanedione (II) in ether/isopentane mixed solvent (1:1 by volume). (—) Spectrum at 300°K in a degassed fluid solvent. The dotted portion of the emission spectrum illustrates the effects of aeration and discriminates the readily quenched phosphorescence from the fluorescence. Where no dotting is shown, the solid and dotted lines are coincident. (- - -) Spectrum at 77°K in a degassed, glassy system. Absorption, fluorescence, phosphorescence, and excitation peaks are discriminated by letters, A, F, P, and EXC, respectively. The excitation wavelength used in all instances was 430 mμ.

associable with a carbonyl carbon–carbonyl carbon stretching mode, and a 1670-cm^{-1} interval associable with the symmetric carbonyl stretching mode.[13] The fluorescence of II is quite weak and the phosphorescence is poorly resolved, consisting of an intense but quite diffuse origin band and a weak shoulder some 1500 cm^{-1} to the red of the origin. The luminescences are of $^{1,3}\Gamma_{n\pi^*} \rightarrow {}^1\Gamma_1$ type;[14] this conclusion is based on (i) the coincidence of origin bands of fluorescence and absorption for I in fluid media at 300°K; (ii) the mirror-image relationship of the same fluorescence and absorption spectra as is specified in i; (iii) the observed lifetimes at 77°K (2–6 msec; see Table II) of the emissive processes typified as phosphorescences; (iv) the presence of the symmetric carbonyl stretching mode in all observed emissions; and (v) the interval of $\sim$2000 cm^{-1} between the origins of phosphorescence and fluorescence emissions.

The emission excitation spectra for I are generally coincident with the absorption spectra and are not shown. This is also true in the case of II, except for fluid media at $\sim$300°K (see Figure 6). In the case of

fluid media, the phosphorescence excitation spectrum of Figure 6 exhibits a displacement toward longer wavelengths in such a way that the excitation maximum appears to become coincident with the red-edge structure previously noted in the absorption of Figure 4. This coincidence suggests that the excitation of planar propanedione molecules is more efficient in the production of phosphorescence than is excitation of the statistically dominant, twisted propanediones. Since all known α-dicarbonyls emit only from the planar (or nearly planar) dicarbonyl geometric configuration[b,10,15] and since all α-dicarbonyls which have been investigated and which cannot attain such planar (or nearly planar) configurations do not emit,[16] it seems reasonable to suppose that CO/CO twisting is conducive to both S$_1$ and T$_1$ energy dissipative processes. It is such effects, presumably, which are responsible for the weak fluorescence of II.

The nonfluorescence of both compounds at 77°K is not understood and is rationalized here by the assumption that much of the 300°K fluorescence capability is

(13) These vibrational intervals correlate clearly with those observed in camphorquinones. See ref 5.

(14) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1967.

(15) (a) T. R. Evans and P. A. Leermakers, J. Amer. Chem. Soc., 89, 4380 (1967); (b) D. J. Morantz and A. J. C. Wright, J. Chem. Phys., 53, 1622 (1970); (c) ibid., 54, 692 (1971).

(16) (a) D. B. Larson and S. P. McGlynn, J. Mol. Spectrosc., 47, 469 (1973); (b) J. F. Arnett and S. P. McGlynn, unpublished results.

Table III. Ionization Potentials of n_+ and n_- Electrons[a]

Molecule	$I(n_+)$, eV	$I(n_-)$, eV	$\Delta_{\pm}$
Glyoxal (C_{2h})	10.52 (10.59)	12.19 (12.19)	1.67 (1.60)
Biacetyl (C_{2h})	9.72 (9.55)	11.63 (11.43)	1.91 (1.88)
Camphorquinone	8.71 (8.80)	10.46 (10.40)	1.75 (1.60)
3,3-Dimethyl-indanedione	8.7	10.8	2.1
Benzil	9.1	11.1	2.0
Oxalic acid	11.20	13.25	2.05
Oxamide	9.80	11.72	1.92

[a] Numbers in parentheses are taken from ref 3 of text.

the result of $S_1 \twoheadleftarrow T_1$ thermally activated events such as have been established[17] for IV.

As is evident from Figures 6 and 7 and Table II, a decrease of temperature from 300 to 77°K usually results in a blue shift of absorption and phosphorescence spectra. This phenomenon appears to be general for all α-dicarbonyls, having been observed by us[16b] for the diaromatics mesitil, phenyl mesityl diketone, and benzil and by others[18] for the absorption spectra of nonaromatic α-diketones. The specific origin of this shift is not obvious to us although conformational changes produced by solvation effects do suggest themselves. In specific, the gross sensitivity of the absorption spectroscopy of α-dicarbonyls to minor variations of the CO/CO dihedral angle and/or steric strain is well known.[10] For example, the release of intramolecular
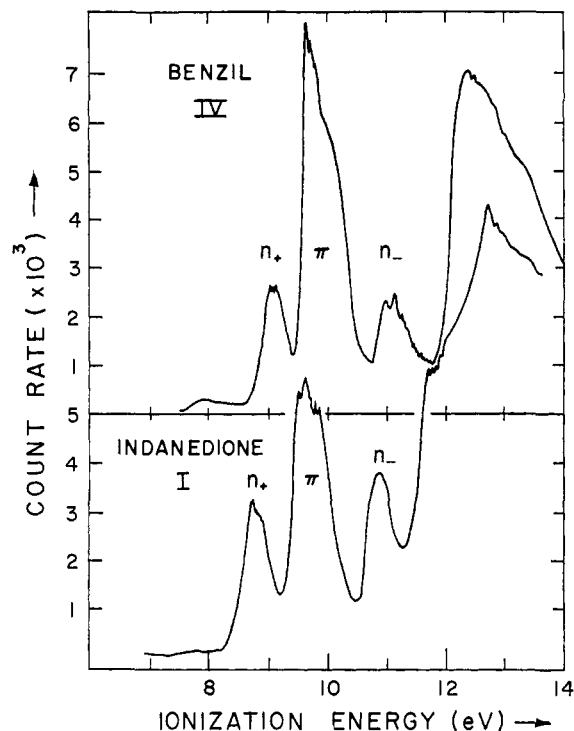

Figure 8. Low-energy photoelectron spectra of benzil and 3,3-dimethylindanedione. The n_+ and n_- notations refer to that previously defined. The π notation refers to an aryl ionization band.

Table IV. A Summary of Experimental Absorption Data and Likely Transition Assignments

Exptl assignment	$\theta = 0°$ cis, synperiplanar 3,3-Dimethylindanedione	$70 < \theta < 110°$ twisted 1-Phenyl-1,2-propanedione	$\theta = 180°$ trans, antiperiplanar Glyoxal
$^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$	18,940, (0, 0), 3-MP		22,200, (0, 0), gas
	19,610, max, 3-MP	24,800, max, 3-MP	22,200, max, gas
$^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$	28,560, (0, 0)?, MCH		28,800, (0, 0), gas
	29,850, max, MCH		33,500, max, gas
$^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$ or $^1\Gamma_{\pi\sigma^*} \leftarrow {}^1\Gamma_1$	32,000, max, 3-MP	34,500, shoulder, 3-MP	
$^1\Gamma_{\pi\pi^*} \leftarrow {}^1\Gamma_1$	36,700, max, 3-MP	38,700, max, 3-MP	

strain occasioned by proceeding from the bicyclic VI to the relatively strain-free VII produces[19] a very large shift of ca. -3000 cm^{-1}. Hence, we assume here that slight changes of the CO/CO dihedral angle, θ, enforced by solvation effects associable with cooling, are responsible for the observed shifts. The effects of cooling on phosphorescence excitation spectra, vis-à-vis blue or red shifting, is difficult to determine in the case of II because of the higher efficiency of phosphorescence of the planar form of II. This difficulty does not exist in I where a distinct blue shift of the phosphorescence excitation spectrum is observed at 77°K.

Photoelectron Spectra. Examples of low-energy portions of photoelectron spectra are shown in Figure 8 for a diaromatic, IV, and a monoaromatic, I, α-dicarbonyl. The n ionizations are distinguished from aromatic π ionizations on the basis of intensity. For example, in IV, which contains two aromatic residues, the ratio of areas π/n_+ is $\sim 4/1$, whereas in I, which con-

tains only one aromatic residue and, hence, only half the π ionizations of IV at ~ 10 eV, the same ratio of areas is $\sim 2/1$. The n_+ and n_- identifications are further established by comparison to biacetyl spectra,[20] where no such π ionizations intrude, to computational results based on Koopmans' theorem (vide infra), and to benzaldehyde spectra[21] where n and π orbitals are nearly degenerate. Results are tabulated in Table III.

Discussion

A synopsis of experimental data and the electronic transition assignments based thereon is given in Table IV. Data on glyoxal are also included in order to encompass the 180° extremum of the CO/CO dihedral angle.

A comparison[5] of the spectra of the indanedione I and its aliphatic analog, 3,3,5,5-tetramethylcyclopentanedione, VII, establishes the independency of the low-energy $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition from the aryl framework

(17) C. A. Parker and T. A. Joyce, J. Chem. Soc. D, 142 (1968).
(18) A. Kuboyama, R. Yanszaki, S. Yabe, and Y. Uehara, Bull. Chem. Soc. Jap., 42, 10 (1968).
(19) J. F. Arnett, D. B. Larson, and S. P. McGlynn, submitted for publication.

(20) J. F. Arnett, J. L. Meeks, and S. P. McGlynn, in preparation for publication.
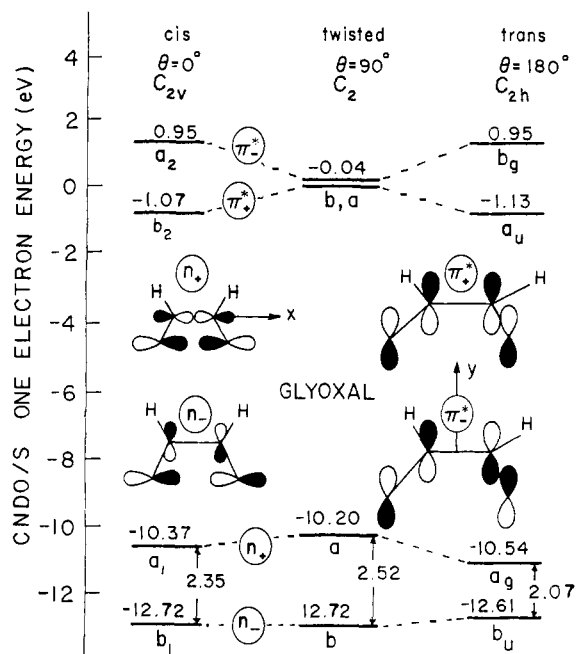(21) J. W. Rabalais and R. J. Colten, J. Electron. Spectrosc., 1, 83 (1972/73).

Figure 9. One-electron MO energies for the n_-, n_+, π_+^*, and π_-^* MO's of glyoxal at twist angles θ = 0, 90, and 180°. The form of the MO's is also schematized for synperiplanar glyoxal. The n_+/n_- separations are indicated at the bottom of the diagram and should be compared with the corresponding experimental separations available in Table III.

of I. The $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition of the indanedione has peaks at 528 and 510 mμ in good correspondence with those of the cyclopentanedione at 538 and 508 mμ. This conclusion is, of course, in full accord with the work of Leonard[22] where the energy of the first $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition is held to be determinative of the CO/CO dihedral angle. In view of this, we accept computations on glyoxal, with θ variable, to be pertinent to a discussion of the two low-energy $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions of both the indanedione I and the propanedione II. The higher energy transitions of these two compounds cannot readily be correlated with any corresponding excitations of aliphatic α-diketones; consequently, these higher energy transitions probably possess significant aryl character and do not fall within the purview of computations based on a glyoxal framework. Therefore, apart from the experimentally based assignments quoted in Table IV, we will not discuss $^1\Gamma_{\pi\pi^*}$ or $^1\Gamma_{n\sigma^*} \leftarrow {}^1\Gamma_1$ excitations any further in this work.

The results of one-electron MO computations are schematized in Figure 9. The MO ordering is the same in all instances (cis, trans and twisted). Furthermore, the n_+/n_- splitting of $\sim$2 eV is seen to be in remarkable accord with the experimental ionization data of Table III and to be more or less independent, experimentally and computationally, of the dihedral angle, θ. In view of this, we now proceed to a one-electron discussion of the electronic absorption spectra.

According to group theoretic considerations only the $\pi_+^* \leftarrow n_+$ and $\pi_-^* \leftarrow n_-$ transitions are electric-dipole allowed. Since only two $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions are observed, it is, therefore, tempting to identify these as the two allowed excitations: $\pi_+^* \leftarrow n_+$ and $\pi_-^* \leftarrow n_-$, in order of increasing energy. In fact, these are the

assignments proposed, for example, by Sidman and McClure[23] for biacetyl, $CH_3COCOCH_3$, and by Maria and McGlynn[25] for dimethyl oxalate, $CH_3OCOCOO\text{-}CH_3$. We will now show that, within the context of one-electron considerations, these assignments are erroneous.

Given the n_+/n_- split of 2.1 eV, the two $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ origin (i.e., 0,0) energies of 18,940 and 28,560 cm^{-1} for the indanedione, and the two assignments, $\pi_+^* \leftarrow n_+$ and $\pi_-^* \leftarrow n_-$ respectively for these two origins, we must conclude that the π_-^* MO is of lower energy than the π_+^* MO. This conclusion is not only in discord with the computational results of Figure 9 but, more importantly, leads to the prediction of a low-energy, electric-dipole forbidden transition of $\pi_-^* \leftarrow n_+$ type at 12,440 cm^{-1}. This prediction discords with the experimental fact of a fluorescence (see Figure 6) which is the inverse of the 18,940 cm^{-1} absorption origin. Consequently, being unwilling to discard the n_+/n_- order which is experimentally well-founded or the validity of Kasha's rule,[14] we are forced to conclude that the absorption origins are best assigned as: $\pi_+^* \leftarrow n_+$ at 18,940 cm^{-1} and $\pi_-^* \leftarrow n_+$ at 28,560 cm^{-1}. This assignment accords[12] with the inverse ellipticities of the 18,940- and 28,560-cm^{-1} origins evident in Figure 5, with the greater antibonding nature of the π_-^* MO as evidenced, we suppose, in the Franck–Condon band shape of the 28,560-cm^{-1} absorption and in the smaller carbonyl stretching frequency which is coupled to this absorption process and with the smaller extinction coefficient of the 28,560-band analog as found in VI[12] and VII.[11]

Similar considerations[16b] of other α-dicarbonyls (i.e., glyoxal, camphorquinone, biacetyl, dimethyl oxalate, etc.) lead to an identical conclusion: Within the one-electron approximation, the two observed $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transitions, in order of increasing energy, are best regarded as $\pi_+^* \leftarrow n_+$ and $\pi_-^* \leftarrow n_+$. Finally, these two transitions should become degenerate in the 90° case (i.e., II or IV) and the expected single $^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition should move toward higher energies in a way reminiscent of the behavior expected for two connected but isolated benzaldehydes. This, of course, is precisely what is observed.[22]

The one-electron picture indulged here could be elaborated in a number of ways which might enhance its credibility but not alter its one inherent defect (i.e., its one-electron nature). Hence, we now introduce electron repulsion considerations and configuration interaction in a two-step sequence. The computations were processed[8] along standard CNDO/s-CI lines and the results are presented in Figure 10 where they are compared with experiment for three representative molecules. As compared with the single-configuration energies (listed under CNDO/s), the state energies (listed under CI) are seen to be in quite remarkable accord with experiment. This accord is all the more remarkable since the computations refer to a glyoxal of variable θ and since we could have substituted camphorquinone for 3,3-dimethylindanedione, benzil for 1-phenyl-1,2-

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(23) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 77, 6471 (1955); see also ref 24.

(24) E. Drent and J. Kommandeur, *Chem. Phys., Lett.*, 14, 321 (1972).

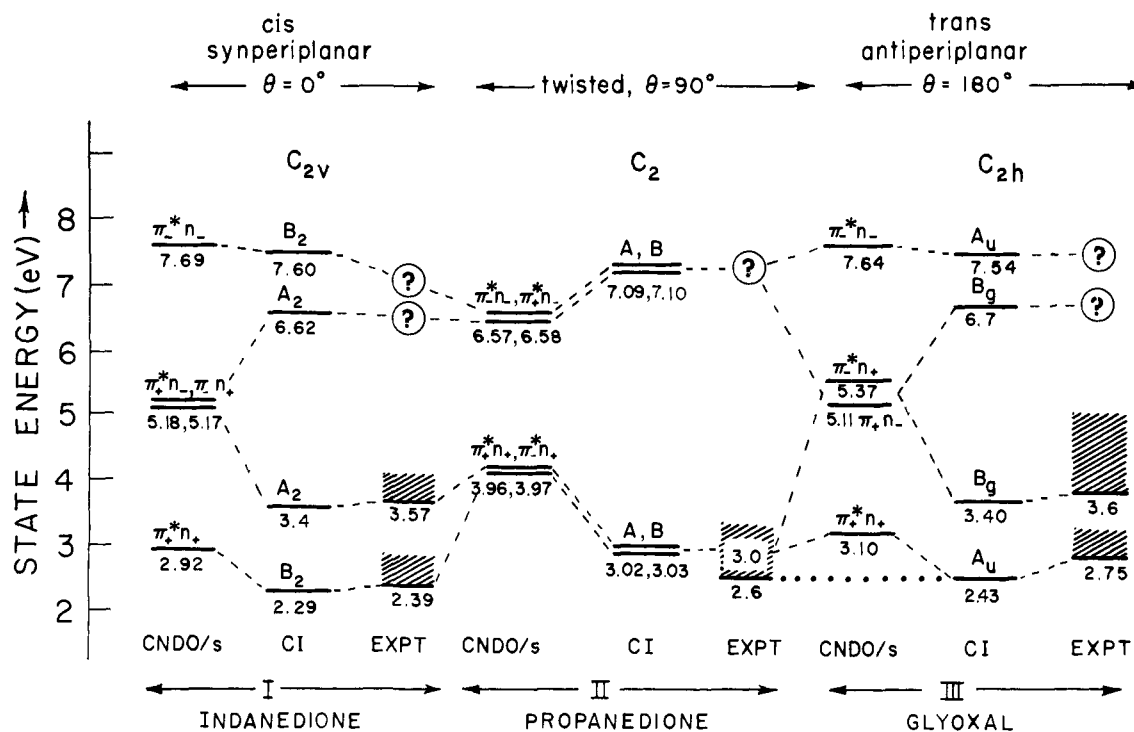(25) (a) H. J. Maria and S. P. McGlynn, *J. Mol. Spectrosc.*, 42, 177 (1972); (b) *ibid.*, 42, 296 (1972).

Figure 10. A correlation of CNDO/s, CNDO/s-CI, and experimental (EXPT) data for the $^1\Gamma_{n\pi}*$ states of α-dicarbonyls at $\theta = 0$, 90, and 180°. The solid line at the bottom of the hashed region under EXPT denotes an origin region, electronic or vibronic as the case may be. The agreement in the case of 1-phenyl-1,2-propanedione is considerably better than is shown. The origin band for the twisted molecule actually lies somewhere in the center of the hashed region (see the discussion under Results), at $\sim$3.0 eV as shown; the bottom of the band at 2.6 eV probably represents the trans form of II and, for that reason, is shown as correlating, *via* a dotted line, with the lowest A_u state of III.

propanedione, mesitil for glyoxal, etc., with no substantive change in the quality of the agreement.

It is tempting to conclude that the many-electron considerations of Figure 10 vindicate also the one-electron schematization of Figure 10 as well as the conclusions derived from Figure 9. This, indeed, is so but a number of reservations must be specified. We will exemplify these by direct reference to synperiplanar glyoxal. The 2.29-eV state of type B_2 does indeed remain largely (*i.e.*, 81%) π_+*n_+. However, the 3.4-eV state of type A_2 is thoroughly mixed, consisting of 49% π_+*n_- and 46% π_-*n_+, as well as other components. In like manner, the 6.62-eV state of type A_2 consists of 44% π_+*n_- and 46% π_-*n_+; whereas the 7.60-eV state of type B_2 consists of 59% π_-*n_- as well as large contaminations of other, more exotic configurational components (*e.g.*, 25% $\pi^*\sigma$). The situation in antiperiplanar glyoxal is, if anything, more complex. And in the twisted 90° case, where π,σ differentiation is lost, the complexity of MO's and states simply invalidates the one-electron view.

The computations agree with experiment in a number of other aspects which follow.

(i) The prediction that the $S_1 \leftrightarrow S_0$ process in synperiplanar glyoxal is of lower energy than that of antiperiplanar glyoxal, in agreement with recent observations by Ramsey, *et al.*[4]

(ii) The prediction that the most stable conformer in the S_0 state is the antiperiplanar conformer (providing that the existence of such a conformer is not sterically or otherwise blocked), in agreement with observation for glyoxal, biacetyl, mesitil, etc.

(iii) The prediction that the twisted S_1 (or T_1) con-

formers are unstable with respect to the S_1 (or T_1) states of either the syn- or antiperiplanar molecules. This prediction implies an ability to rotate intramolecularly as well as the restriction that the S_0 state of the antiperiplanar form be *destabilized* by no more than 0.53 eV relative to the S_0 state of the twisted form or that the synperiplanar form be *destabilized* by no more than 0.67 eV relative to that of the twisted form. Since it is certain that such large, planar conformer destabilizations do not occur except in the presence of specific twisted conformer enforcing chemical bonding, it follows that S_1 or T_1 states of the twisted forms will generally tend to degrade toward corresponding states of one or the other planar forms. In specific, it follows that $S_1 \leftarrow S_0$ excitation of an α-diketone which is twisted in its S_0 state will usually be productive of a planar S_1 (or T_1) excited conformer. This conclusion is in accord with our observations here on the luminescence of II as well as with much previous work.[5,11,16]

(iv) The approximate 50/50 $n_-\pi_+*/n_+\pi_-*$ nature of the second $^1\Gamma_{n\pi}*$ state is in accord with previous experimental arguments[1] which favored a π_-* bonding character for this state.

Conclusion

The discussion given here concerns the configurational excitation nature of the two low-energy $^1\Gamma_{n\pi}* \leftarrow$ $^1\Gamma_1$ transitions which are often observable in the absorption spectra of α-dicarbonyls. The point of view adopted is different from that which is prevalent in the literature and as is exemplified in works by Sidman and McClure,[23] Charney and Tsai,[12] Maria and McGlynn,[25] and Drent and Kommandeur.[24] In order to validate

our present attitudes, we have used experimental data for three α-dicarbonyls which possess quite different CO/CO dihedral angles ($\theta = 0, 90$, and $180°$); we have adduced experimental arguments for heavy $-C(O)C(O)-$ localization of excitation density in the low-energy $^1\Gamma_{n\pi*} \leftarrow {}^1\Gamma_1$ transitions of these α-dicarbonyls; and, as a result, we feel secure in processing quantum chemical computations for glyoxals of variable θ and comparing the results so obtained to experimental data for diaromatic, monoaromatic, and wholly aliphatic α-carbonyls.

In the one-electron MO format, and using Koopmans' theorem, we have been able to rationalize[2] n_+ and n_- ionization potentials. We have also been able to conclude that the standard interpretation[1] (i.e., $^1\Gamma_{n_+\pi_+*} \leftarrow {}^1\Gamma_1$ and $^1\Gamma_{n_-\pi_-*} \leftarrow {}^1\Gamma_1$) of the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions of the simple α-diketones is probably erroneous. This point of view is further vindicated by many-electron computations which include configuration interaction. However, while showing that the standard view has little to sustain it and that the interpretation advanced here is more consistent with the known facts, we do not wish to emphasize this facet of our work. Rather, we prefer to think that we have made a tentative start on a method which should eventually lead to a resolution of the problem posed. That is a study of energy levels, not solely at $\theta = 0, 90$, and $180°$, but over a wide range of θ. In addition, we believe further understanding will result from studies of such series as indanedione, 2,2,4,4-tetramethylcyclobutanedione, 1,4-cyclohexanedione, etc., where the two interacting loci, the $>C=O$ groups, are not only made spatially separate but where the different symmetries also may impose considerably different selection rules on the various $^1\Gamma_{n\pi*} \leftarrow {}^1\Gamma_1$ transitions.

Vapor Phase Excimer Formation in Saturated Amines

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Abstract: The spectral and temporal properties of the excited state of the saturated amine, ABCO (1-azabicyclo-[2.2.2]octane), in the vapor phase are reported. On the basis of these properties, it is shown that ABCO forms an excimer in the vapor phase. This system is analyzed in terms of the usual monomer/excimer kinetic scheme to which one additional rate process had been added, the quenching of the excimer by ground state amine. The rate constants pertaining to the ABCO system are determined by measuring the monomer and excimer decay parameters as a function of the amine vapor pressure. The inference is drawn from solution phase studies that the ABCO excimer is strongly bound and is formed in the head-on approach of two ABCO molecules. The excimer formation efficiency in the vapor phase is determined to be *ca.* 0.2. The effects of added *n*-hexane vapor on the monomer and excimer emission efficiencies and kinetics are examined. Significant excimer enhancement is observed up to *n*-hexane overpressures of *ca.* 90 Torr. This is interpreted in terms of vibrational relaxation (and stabilization) within the monomer and excimer manifolds. The emission intensity and decay data imply that both radiative and nonradiative processes are induced by collisions between ABCO excited monomer and *n*-hexane molecules. The role of termolecular processes in excimer formation is suggested.

The association between ground and excited state molecules (excimer formation) is a well known phenomenon which occurs in the bimolecular electronic relaxation of many aromatic and heteroaromatic molecules.[1] It has been reported recently that certain saturated amines also undergo excimerization, both in the vapor phase and in solution.[2] It appears that vapor phase excimers have not been reported for the aromatic systems, presumably as a consequence of the low vapor pressures which characterize many excimer-forming aromatic molecules at ambient temperatures. At high temperature, where the vapor pressure is high enough to provide a sufficient collision frequency, the concomitant increase in the excimer dissociation rate results in a lower net excimer emission yield.[3]

It is of interest to study the dynamic and energetic properties of the excited monomer and dimer (i.e., excimer) states in the absence of perturbing solvent molecules which affect both the formation and dissociation steps, as well as other nonradiative (and radiative) processes. This paper reports the results of a study of the ABCO, I (1-azabicyclo[2.2.2]octane), excimer in the vapor phase at ambient temperatures.

I

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