of the anthracene anion radical reported by Paul, Lipkin, and Weissman[27] (ϵ 9000 at 14,000 cm^{-1}), R(neutral)/R(dianion) was calculated to be 44. This value was comparable to the observed ratio of the anisotopy factors of both species, g(neutral)/g(dianion) = *ca.* 55.[28] These values support the identification of the dianion and the above assignments of the electronic transition.

The dihedral angle of the DMBA dianion may be given by eq 2. By substituting the intensities of the absorption bands I_- and I_+, which were resolved by reference to each CD maxima, into eq 2, the dihedral angle of the dianion was estimated to be *ca.* 100°. The same value is obtained from the split components of band VI and bands VI_- and VI_+. This value is the same as that of the neutral molecule which is estimated by the same method. In general, it may be expected that the dihedral angle of the dianion may be opened toward trans planar by the electrostatic repulsion force between the MA anion radical moiety. The estimated dihedral angles, however, are not different between the dianion and the neutral molecule. This implies that the MA (or the MA anion radical) moieties in DMBA (or the DMBA dianion) cannot rotate about the 1,1′ band due to large steric hindrance. Indeed any racemization process was not observed both for the neutral molecule and the dianion.

Above discussions can be applied to the dianions which exist in both the triplet state and the singlet state. It is pointed out in the literature that the dianion exists in the triplet state only when the dianion has higher symmetry than D_{2d}.[21,29] The dianions of bis(2,2′-biphenyl)methane[29] and 9,9′-bianthryl[21] exist in the triplet state, since they contain two planar conjugated systems which are perpendicular to each other. In the case of the DMBA dianion, any esr signal was not observed in the green glassy solution. This indicates that the DMBA dianion exists in the singlet state, which corresponds with the fact that the dihedral angle of the DMBA dianion is not 90° but *ca.* 100°.

Acknowledgments. We wish to thank Professor M. Matsuda, Dr. Y. Ikegami, Dr. A. Tajiri, Dr. M. Miyashita, and Mrs. I. Itoh for their helpful discussions.

(27) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

(28) The smaller value of the observed ratio indicates that the observed CD magnitude of the DMBA dianion was smaller than that of the DMBA neutral molecule, since the smaller the splitting energy with the dipole–dipole interaction the larger the compensation of the CD magnitudes with the opposite signs.

(29) R. D. Cowell, G. Urry, and S. I. Weissman, *J. Chem. Phys.*, **39**, 2028 (1963).

Low-Lying Electronic States of Biacetyl

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Abstract: Absorption and emission spectra of biacetyl-h_6 in the visible region have been reexamined at 4–8 K° in the polycrystalline state. The observations in absorption confirm all the important features reported in the 1955 study by Sidman and McClure, and the vibrational analysis of the $^1A_u \leftarrow {}^1A_g$ and $^3A_u \leftarrow {}^1A_g$ band systems, though different in a few details, is similar to that given by these authors. However, the two long-lived emission systems described in the earlier work are due to chemical impurities, and the true $^3A_u \leftarrow {}^1A_g$ phosphorescence is described and analyzed vibrationally. Evidence for an absorption system corresponding to a singlet–singlet electronic transition of a cis or skew rotational isomer is discussed. The biacetyl crystal is photosensitive and the intensity of long-lived impurity emission is enhanced by exposure to wavelengths below 490 nm. The fluorescence and phosphorescence lifetimes measured for crystalline biacetyl-h_6 at 6°K are, respectively, 12 ± 1 nsec and 2.5 ± 0.2 msec.

Although biacetyl (2,3-butanedione) has many photophysical and photochemical applications, its lower excited states have never been fully characterized. The visible absorption of biacetyl (BA) vapor is discrete but extremely complex owing to the thermal distribution of molecules over many levels of the low-lying torsional modes and has not been analyzed.[2a] Our knowledge of the lower electronic states therefore depends on the analysis of the crystal spectrum carried out in 1955 by Sidman and McClure (SM)[3] who established that the principal absorption bands belong to the $\pi^* \leftarrow n_-$ electronic transitions $^1A_u \leftarrow {}^1A_g$ and $^3A_u \leftarrow {}^1A_g$ of *trans*-BA, the 0–0 bands occurring near 437 and 490 nm, respectively, in the solid at low temperatures. Evidence was also obtained for a third absorption system tentatively identified by SM with the singlet–singlet $\pi^* \leftarrow n_+$ electronic transition $^1B_g \leftarrow {}^1A_g$, and an absorption peak at 447 nm (22,359 cm^{-1}) was assigned to a vibronic origin of this system. Although the crystal structure of BA is not known, observations of the factor-group splittings in the vibrational spectrum suggest that *trans*-BA molecules occupy C_i sites in the solid, probably in a C_{2h} space group.[4] In this case the g, u classification of states is rigorous in the crystal and the pure $^1B_g \leftarrow {}^1A_g$ electronic transition is allowed (*xyz* polar-

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(2) G. Herzberg, "Electronic Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1966: (a) p 561, (b) p 538.

(3) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, 77, 6461, 6471 (1955).

(4) J. R. Durig, S. E. Hannum, and S. C. Brown, *J. Phys. Chem.*, **75**, 1946 (1971).

izations) only as a magnetic dipole transition. In this and the following discussion we use the nonrigorous C_{2h} classification since all evidence points to weak intermolecular forces in the solid.

The low-temperature emission of BA is complex. SM reported (a) a fluorescence, $^1A_u \rightarrow {}^1A_g$, based on the 437-nm absorption origin, (b) a "weak" phosphorescence attributed to the $^3A_u \rightarrow {}^1A_g$ transition, and (c) a "strong" phosphorescence provisionally assigned to a vibronic subsystem of the intersystem transition $^3B_g \rightarrow {}^1A_g$. In sum, therefore, the SM results indicate two low-lying excited singlet states, ^1A_u and ^1B_g, and two triplet states, ^3A_u and ^3B_g, the separation of A_u and B_g states being of the order of several hundred reciprocal centimeters in both the singlet and triplet manifolds. This conclusion is by no means improbable; the $n\pi^*$ states of benzoquinone, for instance, have essentially this organization[5] though recent calculations indicate that the n_+,n_- orbital splitting in α-diketones may be much larger, of the order 1–3 eV.[6] However, there are difficulties connected with the dual phosphorescences reported by SM since (i) the "weak" phosphorescence does not show the expected mirror-image relationship to the $^3A_u \leftarrow {}^1A_g$ absorption and cannot be analyzed using the known vibration frequencies of *trans*-BA; and (ii) preliminary measurements in these laboratories have shown that the lifetime of the "weak" (higher frequency) phosphorescence is *greater* than that of the "strong" (lower frequency) phosphorescence. Further, in view of the observation of electronic[7] and microwave[8] absorption due to the cis conformation of the related molecule glyoxal, CHO·CHO, the possibility must be considered that a cis (or skew) isomer contributes to the absorption. The spectrum has therefore been reexamined in an attempt to settle these questions.

Experimental Section

Commercial BA (Fluka) was purified by fractional distillation at atmospheric pressure; the center cut was recrystallized several times from pentane at low temperature and further purified by glc using a PEG 400 column. The absorption spectrum (350–500 nm), recorded in 0.025- and 1.0-mm cells, remained unaltered through the purification stages. For wavelength measurements the spectrum was photographed in the first order of a 3.4-m spectrograph at a reciprocal dispersion of 0.5 nm/mm, with the sample immersed in liquid He at 4.2°K and the wavelengths measured by comparator relative to the emission lines of an Fe hollow cathode lamp. The intensity profile (curves a and b, Figure 1) was recorded with a Cary spectrophotometer operated at a 0.1-nm bandwidth, with the samples cooled by flowing He gas to about 6°K. The half-width (fwhm) of sharp lines in the absorption of an annealed crystal was 0.15 nm, and frequency measurements are therefore reliable to about 1 cm^{-1}. SM reported a half-width of 0.3 nm, possibly owing to the lower resolution of a prism spectrometer. The emission spectra and lifetimes were determined by dye–laser excitation, as described elsewhere.[9] Wavelengths in emission were determined to about 0.1 nm, and ground state frequency intervals are therefore uncertain to 6–8 cm^{-1}.

BA crystals were grown by cooling the liquid in the optical cell. Slow cooling produced an annealed polycrystal but, except for the spectral line width and relative intensity of "traps," the results were not sensitive to the cooling rate. The long-lived emission depends on the photochemical history of the sample, and material used to record the phosphorescence was therefore freshly purified by glc and handled at low-light levels, in the absence of oxygen.

The spectrum of BA-d_6, reported by SM, was not reexamined in this work.

(5) H. P. Trommsdorff, *J. Chem. Phys.*, **56**, 5358 (1972).

(6) J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970); W. Hug, J. Kuhn, K. J. Seibold, H. Labhart, and G. Wagniere, *ibid.*, **54**, 1451 (1971); T.-K. Ha and W. Hug, *ibid.*, **54**, 2278 (1971).

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

(8) J. R. Durig, C. C. Tong, and Y. S. Li, *J. Chem. Phys.*, **57**, 4425 (1972).

(9) J. Ferguson and A. W.-H. Mau, *Aust. J. Chem.*, **26**, 1617 (1973).

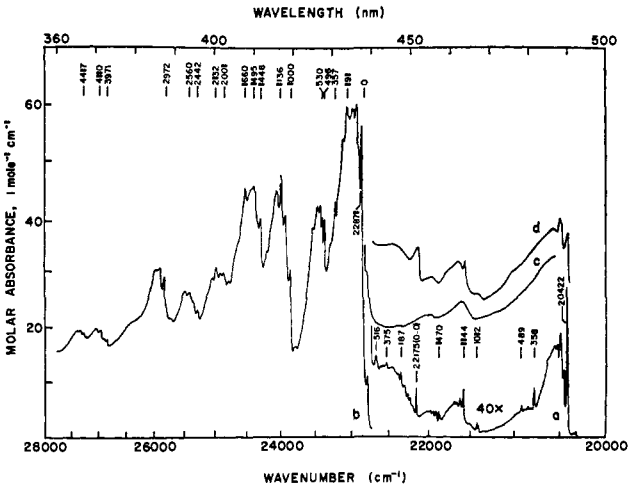

Figure 1. Absorption and photoexcitation spectra of polycrystalline biacetyl. Curves a and b are absorption spectra; curves c and d are photoexcitation spectra (Xe arc excitation, 1.5-nm bandwidth). Curve c is the photoexcitation monitored by the intensity of emission from the ^3A_u state (20,327-cm^{-1} band). Curve d is photoexcitation monitored by impurity emission (19,805-cm^{-1} band). Note that the 450-nm system does not contribute to the ^3A_u emission.

Results and Discussion

(1) The 437-nm System. The absorption spectra recorded in this series confirm all the important features described by SM. The vibrational analysis of the $^1A_u \leftarrow {}^1A_g$ system given in Table I is also essentially equivalent to the SM analysis, except that we have assigned a portion of the intensity to vibronic $^1B_u \leftarrow {}^1A_g$ subsystems, based tentatively on b_g fundamentals of 530 and 1315 cm^{-1} in the electronic ^1A_u state. Of these two fundamentals the $\nu_{20}(b_g) = 530$ cm^{-1} assignment is the more definite,[10] first because it is supported by the activity of the ground state mode $\nu_{20}''(b_g) = 615$ cm^{-1} in the fluorescence spectrum, and second because the ν_{20} mode of *trans*-BA is the analog of the $\nu_8(b_g)$ mode of *trans*-glyoxal which is likewise active in vibronic intensity transfer from the $\pi\pi^*$ to the $n\pi^*$ band systems of that molecule.[2b] The lattice modes, regarded by SM as multiples of a 35-cm^{-1} frequency, are here assigned frequencies of about 40, 71, 109, 135, and, possibly, 154 cm^{-1}.

A medium-intense absorption band at 0 + 2560 cm^{-1} is difficult to assign; from internal evidence it belongs to the $^1A_u \leftarrow {}^1A_g$ system, yet 2560 cm^{-1} is not a combination or overtone of observed fundamentals. We suggest it may be the overtone of the excited-state b_u CO-stretching fundamental and hence that $\nu_{24}'(b_u) \simeq 1280$ cm^{-1}. In the a_g species, the excited state CO-stretching coordinate appears to be strongly coupled with a methyl group motion, probably the symmetric rocking coordinate, so that *two* fundamental vibrations, 1136 and 1448 cm^{-1}, are active in absorption. The average of these two frequencies, about 1290 cm^{-1}, is close to the frequency attributed to the b_u funda-

(10) The notation of ref 4 is used to index the vibrational modes of *trans*-BA, the structure of the representation being $10a_g + 6a_u + 5b_g + 9b_u$.

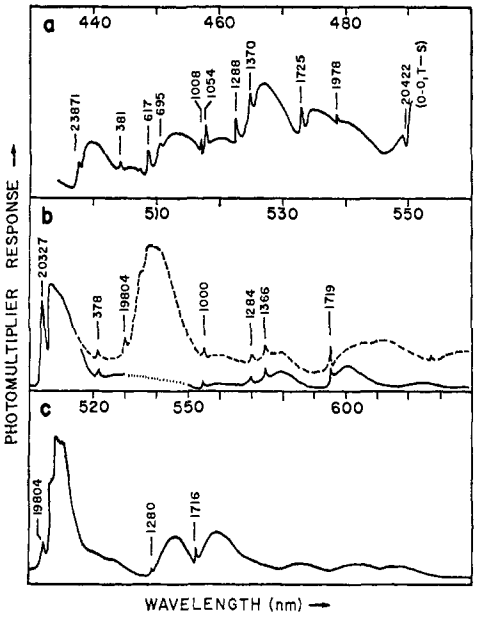

Figure 2. Curve a: fluorescence spectrum, 435–490 nm. Self-absorption occurs near the singlet–singlet and triplet–singlet origins. Curve b: phosphorescence spectrum, 490–560 nm. Broken curve, total long-lived emission; full curve, $^3A_u \leftarrow {}^1A_g$ emission after subtraction of the contribution from the 19,804-cm^{-1} component. Curve c: 19,804-cm^{-1} emission system. Spectra were recorded at 6°K with approximately a 0.2-nm bandwidth and are uncorrected for photomultiplier response.

mental. The vibrational spectrum of the ground state shows that the skeletal motions couple strongly with appropriate modes of the methyl groups.[4]

The vibrational analysis of the fluorescence is summarized in the upper portion of Table I. This analysis is straightforward except for a medium-intense band at 0–1054 cm^{-1}; otherwise, the intervals correlate satisfactorily with the Raman-active fundamentals of *trans*-BA measured at low temperature in the solid state by Durig, Hannum, and Brown.[4] It is possible that the 21,817 (0–1054) cm^{-1} band belongs to a different electronic transition (see below). The profile of the fluorescence system is shown in Figure 2a. The 0–0 band is strongly self-absorbed.

The fluorescence lifetime at 6°K is found to be 12 ± 1 nsec for 420-nm excitation. A recent measurement of the low-pressure lifetime in the vapor state gives 6–14 nsec for 372–445-nm excitation.[11]

(2) The 490-nm System. The first 1500 cm^{-1} of this system in absorption (curve a, Figure 1) closely resembles the 437-nm system. The separation of origins (2449 cm^{-1}) relative intensity, and similar vibrational structure in these two systems is consistent with assignments to the related singlet–singlet and triplet–singlet transitions $^{1,3}A_u \leftarrow {}^1A_g$.

Details of the vibrational analysis are given in Table II. The assignment of the upper-state 517-cm^{-1} frequency to the $\nu_{20}'(b_g)$ fundamental, hence of a vibronic spin–orbit mode of intensity borrowing, is made by analogy with the interpretation of the 530-cm^{-1} mode of the ^1A_u state. This suggestion is speculative. Table III summarizes the assignments from the electronic spectrum relating to the $^{1,3}A_u$ excited states and the ^1A_g ground state of *trans*-BA.

(11) G. M. McClelland and J. T. Yardley, *J. Chem. Phys.*, **58**, 4368 (1973).

Table I. Absorption and Fluorescence of Biacetyl-h_6, ^1A_u–^1A_g

ν,[b] cm^{-1}	$\Delta\nu$, cm^{-1}	Assignment[a]
		Fluorescence
20,893	−1978	1367 + 614 = 1981
21,146	−1725	a_g fundamental (1719 R, p)
21,426	−1445	lattice; −1370 − 75
21,501	−1370	a_g fundamental (1367 R)
21,583	−1288	a_g (or b_g) fundamental (1288 R)
21,742	−1129	Lattice; −1054 − 75
21,817	−1054	?
21,863	−1008	a_g fundamental (1001 R, p)
22,176	−695	a_g fundamental (693 R, p)
22,254	−617	b_g fundamental (614 R, dp)
22,343	−528	a_g fundamental (526 R, p)
22,420	−451	Lattice; −381 − 70
22,490	−381	a_g fundamental (380 R, p)
		Absorption
22,805	−66	Trap
22,845	−26	Trap
22,871	0	Origin
22,911	40	
22,942	71	Lattice
22,980	109	
23,006	135	
23,062	191	A_g; 2 × acetyl torsion
23,288	357	a_g fundamental
23,367	496	a_g fundamental
23,401	530	b_g fundamental
23,436	565	Lattice; 496 + 69
23,466	595	Lattice; 496 + 100, 530 + 65
23,722	851	A_g; 357 + 496 = 853
23,756	885	B_g; 357 + 530 = 887
23,793	922	Lattice; 851 + 71
23,871	1000	a_g fundamental
23,911 sh	1040	Lattice; 1000 + 40
23,942	1071	Lattice; 1000 + 71
23,975 sh	1104	Lattice; 1000 + 104
24,008	1136	a_g fundamental
24,045 sh	1174	Lattice; 1136 + 38
24,074	1203	Lattice; 1136 + 67
24,110 sh	1239	Lattice; 1136 + 103
24,185	1314	b_g fundamental (?)
24,223	1352	A_g; 1000 + 357 = 1357
24,249	1378	Lattice; 1314 + 64
24,275	1404	Lattice
24,319	1448	a_g fundamental
24,366	1495	A_g; 1000 + 496 = 1496: 1136 + 357 = 1493
24,387	1516	Lattice; 1448 + 68
24,403	1532	Lattice; 1495 + 37
24,531	1660	B_g; 530 + 1136 = 1666
24,592 sh	1721	Lattice; 1660 + 61
24,675	1804	A_g; 356 + 1448 = 1804
24,810	1939	A_g; 496 + 1448 = 1944
24,872	2001	A_g; 2 × 1000 = 2000
24,925	2054	Lattice
25,003	2132	A_g; 1000 + 1136 = 2136
25,068	2197	Lattice; 2132 + 65
25,313	2442	A_g; 1000 + 1448 = 2448
25,431	2560	A_g; 2 × 1280 (b_u) (?)
25,491	2620	Lattice; 2560 + 60
25,782	2911	A_g; 357 + 2560 = 2917
25,843	2972	a_g fundamental
25,913	3042	Lattice; 2972 + 70
25,946	3075	Lattice; 2972 + 103
26,199	3328	A_g; 356 + 2972 = 3328
26,338	3467	A_g; 496 + 2972 = 3468
26,842	3971	A_g; 1000 + 2972 = 3972
26,981	4110	A_g; 1136 + 2972 = 4108
27,288	4417	A_g; 1448 + 2972 = 4420

[a] In parentheses, Raman frequencies of Durig, Hannum, and Brown.[4] [b] sh = shoulder.

Immediately to the red of the 0–0 band in absorption 20,422 cm^{-1}) there are two weak features, at 20,348 and 20,364 cm^{-1}, whose intensity is sharply affected by

Table II. Absorption and Phosphorescence of Biacetyl-h_6, ^3A_u–^1A_g

ν, cm^{-1}	$\Delta\nu$, cm^{-1}	Assignment[a]
		Phosphorescence[b]
18,608	−1719	a_g fundamental (1719 R, p)
18,897	−1430	Lattice; −1336 − 64
18,961	−1366	a_g fundamental (1367 R)
19,043	−1284	a_g fundamental (1288 R)
19,327	−1000	a_g fundamental (1001 R, p)
19,949	−378	a_g fundamental (380 R, p)
20,168	−159	Lattice
20,193	−134	
20,222	−105	
20,257	−70	
20,288	−39	
20,327	0	0–0 band, emission
		Absorption
20,348	−74	Trap
20,364	−58	Trap
20,422	0	0–0 band, absorption
20,463	41	
20,488	66	Lattice
20,498	76	
20,525	103	
20,558	136	
20,615	193	A_g; 2 × acetyl torsion
20,780	358	a_g fundamental
20,818	396	Lattice; 358 + 38
20,848	426	Lattice; 358 + 68
20,858	436	Lattice; 358 + 78
20,880	458	Lattice; 358 + 100
20,911	489	a_g fundamental
20,938	516	b_g fundamental (?)
20,978	556	Lattice; 489 + 67; 516 + 40
21,422	1000	B_g; 489 + 516 = 1005
21,434	1012	a_g fundamental
21,473	1051	Lattice; 1012 + 39
21,498	1076	Lattice; 1012 + 64
21,566	1144	a_g fundamental
21,603	1181	Lattice; 1144 + 37
21,632	1210	Lattice; 1144 + 66
21,640	1218	Lattice; 1144 + 74
21,667	1245	Lattice; 1144 + 101
21,700	1278	Lattice; 1144 + 134
21,892	1470	a_g fundamental
21,924	1502	A_g; 358 + 1144 = 1506
21,959	1537	Lattice; 1470 + 67; 1502 + 35
21,992	1570	Lattice; 1470 + 100; 1502 + 68

[a] In parentheses, Raman frequencies measured by Durig, Hannum, and Brown.[4] [b] The region 19,850–19,500 cm^{-1} is obscured by impurity emission.

the thermal treatment of the sample.[12] In an annealed polycrystal these "traps" have about 1/50th the intensity of the main peak, though this ratio is closer to 1/10 in a rapidly frozen sample. We attribute these peaks to the 0–0 transition of molecules in abnormal locations, for example, on surface sites or in a microcrystal of different habit from the bulk material. They are the only spectral features strongly affected by the rate of cooling and are not considered significant in a classification of free-molecule transitions.

(3) Phosphorescence of BA-h_6. The $^3A_u \rightarrow {}^1A_g$ emission of BA does not correspond with the "weak green" or the "strong green" phosphorescences described by SM.

A relatively impure sample, distilled once from the commercial product, gives rise to the "strong green" and "weak green" phosphorescences described by SM. The higher frequency "weak green" emission can be

(12) Similar "traps" occur to the red of the 0–0 band of $^1A_g \leftarrow {}^1A_u$, at 22,805 and 22,845 cm^{-1}.

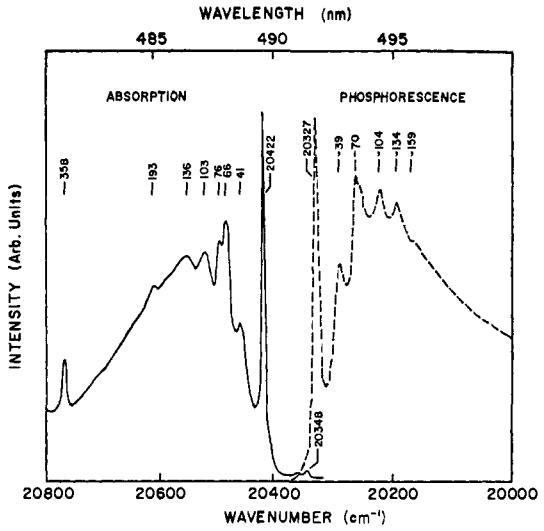

Figure 3. 0–0 bands and lattice-mode structure in the ^3A_u–^1A_g transitions.

Table III. Band Origins, Lifetimes, and Vibrational Frequencies of *trans*-Biacetyl

	^1A_u–^1A_g system	^3A_u–^1A_g system	Solid state vibrational spectrum[a]
ν_0, cm^{-1}	22,871	20,422	
Lifetime, 6°K[b]	12 ± 1 nsec	2.5 ± 0.2 msec	
	Ground State Fundamentals (±6 cm^{-1})		
	1725	1719	1719 ν_3 (a_g)
	1370	1366	1367 ν_5 (a_g)
	1288	1284	1288 ν_6 (a_g)
	1008	1000	1001 ν_7 (a_g)
	695		693 ν_8 (a_g)
	617		614 ν_{20} (b_g)
	528		526 ν_9 (a_g)
	381	378	380 ν_{10} (a_g)
	Excited State Fundamentals (±1 cm^{-1})		
	2972		CH stretch (a_g)
	1448	1470	CO stretch
	1136	1144	+ CH_3 rock (a_g)
	1000	1012	CC stretch (a_g)
	530	516	$COCH_3$ wag (b_g)
	496	489	$COCH_3$ bend (a_g)
	357	358	$COCH_3$ rock (a_g)
	191	193	2 × $COCH_3$ torsion (A_g)

[a] Reference 4. [b] $\Phi_F/\Phi_P \approx 0.01$.

followed only to the onset of "strong green" emission (19,804 cm^{-1}) which, in the impure crystal, is at least one order of magnitude more intense than the "weak" system. Neither the "strong green" nor the "weak green" emission shows a phonon structure remotely similar to that seen in absorption.

Fractional distillation and/or glc modifies the emission considerably. The original "weak green" emission, characterized by prominent bands at 20,119, 20,028, and 19,991 cm^{-1}, vanishes and is replaced by a band at 20,327 cm^{-1} possessing a mirror-image relationship to the 0–0 band of the triplet–singlet transition in absorption (see Figure 3).[13] Further, the intensity of the "strong green" emission is very much reduced. A

(13) The 20-327-cm^{-1} band is included by SM in the "weak green emission" but was observed only with low intensity.

profile of the long-lived emission from the purified crystal is shown in Figure 2b.

The reduced intensity of the 19,804-cm^{-1} emission exposes additional bands of the 20,237-cm^{-1} system as listed in the top portion of Table II. These bands are readily analyzed in terms of the Raman-active fundamentals of *trans*-BA in the crystal state and this analysis, together with the similarity of the absorption and emission profiles, is definite physical evidence that the new system is the authentic $^3A_u \rightarrow {}^1A_g$ phosphorescence. The 95-cm^{-1} gap between the 0–0 bands in absorption and phosphorescence indicates that the emission occurs only from molecules in certain disordered sites. At 6°K, the measured lifetime of the ^3A_u emission is 2.5 ± 0.2 msec.

We next consider the source of the "strong green" emission. Its decay is nonexponential, the initial portion of the decay curve corresponding to a lifetime of 1.3 ± 0.1 msec. Compared with the 20,327 system, therefore, the lower energy emission has the *shorter* lifetime, so that the emitter cannot be the same for both. Moreover, the intensity of this "strong green" system is minimized (though not successfully eliminated) by conducting the purification and transfer of BA at low-light levels, suggesting that the impurity is formed by irradiation of BA. This conclusion is supported by the following observations: (i) provided the sample is kept at about 6°K the relative intensity of 20,327- *vs.* 19,804-cm^{-1} emission is unchanged by prolonged irradiation with the dye laser; however, (ii) if the irradiated sample is cycled through room temperature the intensity of the 19,804-cm^{-1} emission is increased *irreversibly* by an order of magnitude; and (iii) the 19,804-cm^{-1} intensity varies sharply with temperature in the range 6–12°K, the 19,804-cm^{-1} emission intensity being favored *reversibly* by the higher temperature. These events support the photochemical formation of a trapped intermediate which does not contribute to the 6°K emission but which reacts further to produce molecules responsible for the "strong green" emission unless the irradiated sample is kept at low temperature. The reversible intensity shift between 6 and 12°K indicates that the energy transfer from the ^3A_u state of *trans*-BA to this impurity involves a passage across a low-energy barrier.

(4) The 450-nm System. The region 440–450 nm shows increasing absorption intensity between the peak at 22,175 cm^{-1} (451 nm) and the onset of strong absorption associated with the 437-nm system (curve a, Figure 1). SM established that perdeuteration shifts the 22,175-cm^{-1} peak by +15 cm^{-1}, the order of magnitude of an origin isotope shift.[14] Since the 22,175-cm^{-1} band does not fit the vibrational analysis of the $^3A_u \leftarrow {}^1A_g$ system we believe that it must be assigned to the 0–0 band of a third electronic band system.[15]

Curve c, Figure 1, gives the photoexcitation spectrum of the 490–440-nm region, monitored by the intensity of the 20,327-cm^{-1} $^3A_u \rightarrow {}^1A_g$ phosphorescence. Evidently the 450-nm system does not contribute to the ^3A_u emission, even though it contributes strongly to the 19,804-cm^{-1} impurity emission as shown in curve d of Figure 1. Therefore, the 450-nm state undergoes energy transfer to the impurity in preference to a relaxation to ^3A_u. The evaluation of this evidence is speculative, but we believe the results are best explained by attributing the 440–450-nm absorption to the electronically allowed $^1B_1 \leftarrow {}^1A_1$ transition of *cis*-BA.[16] This explanation indicates that the BA polycrystals used in this work were disordered, with some of the cis conformation trapped in a trans host. If this is granted the absorption intensity of the cis rotamer (more than two orders of magnitude less than that of the 437-nm *trans*-BA intensity) corresponds to <1% of cis doping in the trans crystal, assuming equal absorption intensities. This is consistent with the failure to detect *cis*-BA in the vibrational spectrum of solid and liquid biacetyl.[4]

The vibrational structure of this system extends to three bands at 22,362 (0 + 187), 22,250 (0 + 375), and 22,689 (0 + 514) cm^{-1}, possibly related to the 191-, 357-, and 496-cm^{-1} frequencies of *trans*-BA in the ^1A_u state. The "extra" band in fluorescence spectrum, 21,817 cm^{-1}, may also belong to this system. A second fluorescence band, at 22,176 cm^{-1}, coincides with the 0–0 band of the cis system though in this case an alternative assignment is available (Table I).

Relaxation processes in the crystal tend to bypass the upper state of the 450-nm bands. Excitation into the ^1A_u system, for instance, leads to rapid relaxation to ^3A_u, the measured value of the relative quantum yields of fluorescence and phosphorescence being $\Phi_F/\Phi_P \simeq 0.01$. The upper state of the 450-nm system behaves quite differently; excitation into this state is *not* followed by a radiationless transition to ^3A_u (curve c, Figure 1), nor does excitation into the ^1A_u system lead to more than a possible small fraction of fluorescence from the upper state of the 450-nm bands. These observations indicate that the 450-nm system cannot belong to *trans*-BA and hence that these bands should not be assigned to the magnetic dipole transition $^1B_g \leftarrow {}^1A_g$, the interpretation favored by SM.[4] The ^1B_g state may well be associated with the 315-nm band system in the ultraviolet region.

If, however, the 450-nm bands are assigned to the $^1B_1 \leftarrow {}^1A_1$ transition of *cis*-BA, any reasonable estimate of the cis–trans energy difference in the ground state (>1000 cm^{-1}, say) places the $^1B_1$ state of *cis*-BA at higher energy than the ^1A_u state of the trans isomer. Granted this, it is easy to see why excitation into the ^1A_u bands is then followed by relaxation to ^3A_u instead of the excited state of the 450-nm system.

Conclusion

The vibrational-electronic spectrum of *trans*-biacetyl for visible wavelengths has been reexamined in the solid state at 4–6°K, and the results have been interpreted in terms of transitions from the ground state to the first excited states of the singlet and triplet manifold, $^{1,3}A_u \leftarrow {}^1A_g$. The separation of ^1A_u and ^3A_u states is 2449 cm^{-1} in the crystalline state. A third, weak absorption system near 450 nm is attributed tentatively to the $^1B_1 \leftarrow {}^1A_1$ (or $^1B \leftarrow {}^1A$) electronic transition of cis (or skew) biacetyl molecules trapped in a

(14) The origin isotope shift in the ^3A_u–^1A_g transition is +17 cm^{-1} (ref 3).

(15) The 22,175-cm^{-1} band was assigned by SM to the CO-stretching motion in the ^3A_u state, ν_{CO} = 1723 cm^{-1}. However, this frequency is unreasonably high.

(16) The expression *cis*-BA used to describe the rotational isomer is not precise. For steric reasons the equilibrium configuration may prefer a skew structure.

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.

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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 (θ = 0°) α-diketone, 3,3-dimethylindanedione (I), and a twisted (70 < θ < 110°) α-diketone, 1-phenyl-1,2-propanedione (II). We accept the available data[4] for an antiperiplanar (θ = 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

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