authentic **6** on four different columns (10% SE-30, 15% XF-1150, 15% FFAP, and 15% Carbowax 20M). The nmr spectrum of an impure sample of diketone showed all the bands corresponding to the authentic material (as well as some impurity absorptions).

***endo*,*endo*-2,6-Dicarboxy-*cis*-bicyclo[3.3.0]octane (7).** The output of a Welsbach Model T-408 Ozonator was bubbled through an ice-cold solution of 0.78 g of V in 50 ml of 90% acetic acid until the exhaust gases turned a 2% potassium iodide solution dark brown. After addition of 4.5 ml of 40% peracetic acid in acetic acid to the ice-cold, stirred solution, the mixture was heated to reflux for 2 hr. The acetic acid was removed to give a quantitative yield of a moist, white solid which was recrystallized from water to yield 0.36 g (38%) of **7** as a white, crystalline solid, mp 222–225°; infrared (Nujol): 3–4 and 5.9 μ. A second recrystallization from water gave an analytical sample, mp 222–223°.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.48; H, 7.18.

Equilibration of *endo*,*endo*-2,6-Dicarbomethoxy-*cis*-bicyclo[3.3.0]-octane (8). The diacid **7** (0.36 g) was esterified with diazomethane in the usual manner to give 0.43 g of **8** as a yellow oil. Molecular distillation gave a colorless oil; infrared: 5.77 μ; nmr ($CDCl_3$): a sharp six-proton singlet at δ 3.64 (OCH_3), a broad four-proton multiplet at 2.8 (*CH*), and a broad eight-proton multiplet at 1.7 (CH_2). Glpc analysis showed 90% of the major component **8** plus three minor components.

A solution of 50 mg of this diester in 5 ml of methanol containing a catalytic amount of sodium methoxide was heated to reflux for 28 hr. Glpc assay showed that one minor component was gone, the major component (**8**) was reduced to about 5% of the total sample, and the two other minor components were increased to about 95% of the total product in roughly equivalent amounts. No further change in the product composition was effected by an additional 24 hr of heating. The solution was diluted with 40 ml of water and extracted with three portions of ether. The combined ether solutions were dried, and the solvent was removed to leave a yellow oil. Both the infrared and nmr spectra of this material were similar to, but not identical with, those of **8**, and fully in accord with expectation for a mixture of **9** and **10**.

***cis*-Bicyclo[3.3.0]octane-*endo*,*endo*-2,6-dicarboxylic Acid Anhydride (11).** To a stirred solution of 0.20 g of **7** in 150 ml of dry acetonitrile at room temperature was added a solution of 0.19 g of distilled dicyclohexylcarbodiimide in 25 ml of dry acetonitrile and two drops of pyridine. The solution was stirred for 26 hr at room temperature during which time a white solid precipitated. The solid was removed by suction filtration, and the solvent was evaporated from the filtrate to give *ca.* 100 mg of a colorless oil; infrared: 5.58 and 5.72 μ, and 5.88 μ (diacid). Molecular distillation gave crude **11** as a colorless liquid (~50 mg); infrared: 5.58 and 5.72 μ (second band stronger).

This oil was dissolved in methanol and left at room temperature for 3 days. The methanol was removed and the residue was esterified with diazomethane to give a white semisolid which yielded a colorless oil upon molecular distillation. Glpc examination indicated that the major component (~80%) of this material was identical with **8**; infrared comparison confirmed this conclusion.

Acknowledgments. This work was supported by the Public Health Service in the form of a research grant (GM 12860) and by the National Science Foundation which provided an equipment grant (GP 5234) for the purchase of the mass spectrometer used in this work. The gift of a sample of cyclododecatrienes from the Columbian Carbon Company is acknowledged with pleasure.

Emission Spectra and Excited-State Geometry of α-Diketones

Ted R. Evans and Peter A. Leermakers

Contribution from the Department of Chemistry, Wesleyan University, Middletown, Connecticut 06457. *Received March 29, 1967*

Abstract: Absorption and emission spectra of a series of open-chain and cyclic aliphatic and aromatic α-diketones have been measured. From absorption, fluorescence, and phosphorescence data singlet–triplet splittings have been measured, and scrutiny of absorption and fluorescence curves permits an estimation of conformational differences between ground and emitting excited states.

The geometry of ground states of complex molecules can be qualitatively determined by numerous methods, but few ways exist for determining conformations or geometries of excited states of the same molecules. Often the configuration is assumed to be the same as that for the ground state, or is assumed to be different on the basis of intuition,[1] or is deduced by reasonably elaborate measurements.[2]

Several groups of workers have clearly shown that the n–π* absorption of α-diketones is strongly dependent upon the intercarbonyl dihedral angle of the diketone.[3-9] Leonard and co-workers, in the most extensive study, found that the long wavelength n–π* transition occurred at 420–500 mμ for either cisoid or transoid coplanar dicarbonyl systems, and shifted to substantially higher energies (λ_{max} <400 mμ) whenever the intercarbonyl dihedral angle deviated significantly from 0 or 180°.

Surprisingly the emission spectra of few α-diketones have been reported. Biacetyl has been used in a number of triplet energy-transfer studies because of its property of phosphorescing both in fluid solution at room temperature and in a glass at 77°K.[10-15] The

---

(1) A. S. Cherkasov and K. G. Voldaikma, *Bull. Acad. Sci. USSR, Phys. Ser.*, 27, 630 (1963).

(2) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.* (London), **A275**, 135 (1963).

(3) N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, 72, 5388 (1950).

(4) N. J. Leonard, R. T. Rapala, H. L. Herzog, and E. R. Blout, *ibid.*, 71, 2997 (1949).

(5) N. J. Leonard and E. R. Blout, *ibid.*, 72, 484 (1950).

(6) N. J. Leonard, A. J. Kresge, and M. Oki, *ibid.*, 77, 5078 (1955).

(7) C. Sandris and G. Ourisson, *Bull. Chim. Soc. France*, **25**, 350 (1958).

(8) C. Sandris and G. Ourisson, *ibid.*, 23, 958 (1956).

(9) K. Alder, H. K. Schaffer, H. Esser, H. Krieger, and R. Reubke, *Ann. Chem.*, **593**, 23 (1955).

(10) S. Murov, D. S. McClure, and N. C. Yang, *J. Chem. Phys.*, **45**, 2204 (1966).

(11) J. T. Dubois and M. Cox, *ibid.*, **38**, 2536 (1963).

(12) H. H. Richtol and A. Belorit, *ibid.*, **45**, 35 (1966).

(13) J. T. Dubois and F. Wilkinson, *ibid.*, **39**, 899 (1963).

(14) H. H. Richtol and F. H. Klappmeier, *J. Am. Chem. Soc.*, **86**, 1255 (1964).

Table I

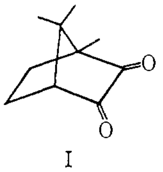
Compd	Long wavelength abs λ_{max}, mμ	$E_{abs}\lambda_{max} - E_{phos}\lambda_{max}$, cm^{-1}	E_T, kcal	ΔE_{S-T}, cm^{-1} [a]	Most probable ground state θ, deg
Biacetyl	422	3200	55.6	2500	180[b]
2,3-Pentanedione	419	3700	55.6	2500	180[c]
Pivalil (II)	370	8500	51.6	2100	110–150[d]
Bornanedione (I)	483	2300	51.6	2100	0–10[d]
1,2-Cycloheptanedione	410	4800	57.5	2600	15–30[e]
1,2-Cyclodecanedione	400	5600	55.5		70–110[e]
Benzil	379	7800	53.0	2700	~90[d]
1-Phenyl-1,2-propanedione	395	6100	54.0		70–110[e]
α-Pyridil	360	5200	59.0	2700	~90[d]
α-Furil	400	6500	55.0	[f]	70–110[e]

[a] The energy difference between the fluorescence and phosphorescence maxima, which should be a reasonable approximation of the true singlet–triplet splitting, *i.e.*, the difference between the respective 0–0 bands. [b] Reference 19. [c] Presumed from the spectral similarity to biacetyl. [d] Values from Leonard, ref 3. [e] Presumed values based on absorption spectra interpolated from Leonard's absorption data. [f] Value not available since these compounds did not fluoresce.

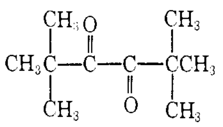
emission spectra of 2,3-pentanedione has been known for over a decade[16] and recently Richtol and Klappmeier published a study of the luminescence of biacetyl, 2,3-pentanedione, and 2,3-octanedione.[17] Benzil, *p*-anisil, and naphthil are the only nonquinoid aromatic α-diketones whose emission spectra have been recorded.[12,15,18] Most of the above aliphatic and aromatic diketones exhibit rather similar emission spectra with weak fluorescence in the 470-mμ region and phosphorescence in the region around 520 mμ at room temperature. At 77°K, in many cases, the fluorescence disappears, and the phosphorescent emission becomes somewhat sharper. The only significant variation in the emission spectra of the homologous *aliphatic* series is that the emission yield decreases with increasing chain length due to intramolecular deactivation.

Results and Discussion

Table I contains absorption and emission spectral data of the α-diketones examined in the present investigation, along with estimated values for the intercarbonyl dihedral angles for each compound *in the ground state.* Also given are energy differences between the absorption and phosphorescence maxima, as well as the differences between fluorescence and phosphorescence maxima (the latter differences being reasonable approximations of the differences between the respective 0–0 bands and thus relatively accurate values for singlet–triplet splittings). Since conjugative and inductive effects are least important in the aliphatic series, biacetyl, bornanedione (I), and pivalil (II) were chosen as model systems.



I



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-\underset{O}{\underset{\|}{C}}-\overset{CH_3}{\underset{CH_3}{C}}CH_3}$$

II

Ground-state bornanedione exists essentially as a *cis*-coplanar dicarbonyl system (dihedral angle θ = 0–10°),[3,7] pivalil exists in a skew configuration (θ = 110–150°),[3,7] and biacetyl is *trans* coplanar (θ = 180°).[19] The long wavelength absorption band maximum of I is at 493 mμ at 77°K and at 483 mμ at room temperature (in both cases the absorption is quite sharp). This small but real shift to the red at low temperature is not observed in open chain diketones studied including biacetyl. I shows weak fluorescence at 495 mμ and strong phosphorescence at 77°K at 550 mμ. The singlet–singlet 0–0 band must be near 495 mμ because of the close overlap in absorption and fluorescence. This gives a singlet–triplet splitting on the order of 2100 cm^{-1} which is slightly smaller than the 2500–3000 cm^{-1} splitting found for glyoxal and biacetyl (*trans*-coplanar emitting states).[19,20]

Pivalil exhibits a very broad long wavelength absorbtion band from 320 to 480 mμ (width 10,400 cm^{-1}) with a maximum at 370 mμ. This is in contrast to that for bornanedione which has a band width of 5400 cm^{-1} in its lowest energy n–π* absorption. The difference in the band widths is undoubtedly a reflection of the range of possible rotational conformers allowed in I and II for Franck–Condon excitation. The band maximum for pivalil does not change in going from room temperature to 77°K, indicating that the conformation of the most probable species remains the same.

The emission of II at 77°K consists of fluorescence at 485 and 515 mμ and phosphorescence at 550 mμ (Figure 1). At room temperature, only the former two peaks are observed with no shift in position. The assignment of the high energy emission peaks as fluorescence was made because of the very short lifetime (at the highest possible speed of the rotating can, the 485- and 515-mμ peaks were not observed at 77°K although the 550-mμ band appeared clearly even at moderate speeds) and because of the following quenching experiment. The phosphorescence of 0.1 *M* biacetyl (E_T = 55 kcal) is totally quenched in a 1:2 *cis*-piperylene (E_T = 56.9)[21]–isopentane glass at 77°K;

---

(15) H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, **14**, 48 (1960).

(16) G. N. Lewis and M. Lewis, *J. Am. Chem. Soc.*, **67**, 994 (1945).

(17) H. H. Richtol and F. H. Klappmeier, *J. Chem. Phys.*, **44**, 1519 (1966).

(18) W. G. Herkstroeter, J. Saltiel, and G. S. Hammond, *J. Am. Chem. Soc.*, **85**, 482 (1963).

(19) J. W. Sidman and D. S. McClure, *ibid.*, **77**, 6461 (1955).

(20) J. D. D. Brand, *Trans. Faraday Soc.*, **50**, 431 (1954).

(21) G. S. Hammond, *et al.*, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

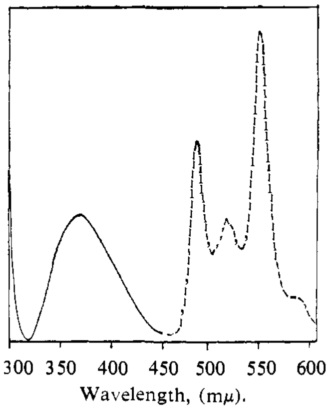


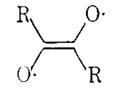
Figure 1. Long wavelength absorption (ϵ_{max} 20), ———, and total emission (relative intensities), - - - -, of pivalil at 77°K.

however, no quenching is observed for either the 485- or the 515-mμ band (the latter corresponding to an excitation energy of 59 kcal) of pivalil in the same matrix. No quenching would be expected, nor was any observed, of the phosphorescent peak because of its low energy ($E_T \sim$ 52 kcal). The energy difference between the singlet formed by Franck–Condon absorption from the most probable ground-state conformation, and the emitting triplet is very large (about 8500 cm^{-1}) compared to normal S–T splittings for n,π states. However, the energy difference between the 485-mμ fluorescence and the phosphorescence at 550 mμ (a reasonable approximation of the energy difference between the respective 0–0 bands) is 2100 cm^{-1} indicating that there is no abnormal configurational difference between the *emitting* singlet and triplet species. The relatively small value of the "singlet–triplet" splitting also indicates that the transition is π^*–n rather that π^*–π.[22,23]

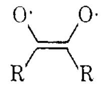
However, the large separation between the absorption and fluorescence bands, and the lack of mirror image symmetry (see Figure 1), demands that there is a significant configurational change between the *most probable* ground-state conformation and the conformation of the relaxed, *emitting* excited singlet (and triplet) states. This "violation" of mirror image symmetry has previously been used to confirm configurational changes in ground and excited states.[2] (In the case of this compound, as in all compounds in Table I, excitation spectra corresponded well enough to absorption spectra to ensure that observed emission was real and not due to impurities or other artifacts.)

Examination of Table I shows that the range in energies (derived from phosphorescence λ_{max}, not 0–0 bands) of the triplet states of the diketones studied is 2400 cm^{-1} (bornanedione–pyridil, 18,000–20,400 cm^{-1}), but the energy range for lowest energy excited singlet states (from absorption λ_{max}) is 7600 cm^{-1}. There are obviously factors other than the intercarbonyl dihedral angle operating in the aromatic and heterocyclic compounds; thus an exact correlation with the aliphatic diketones should not be expected. Yet, the same general trend is observed in aromatic and aliphatic diketones. When the absorption maximum of the diketone is displaced to the blue, indicating a skewed ground state, the energy of the emitting state nevertheless remains relatively constant. This constancy or consistency in the energy of the emitting state suggests that in general α-diketones emit from a coplanar conformation.[18–20]

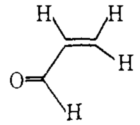
A simple molecular orbital picture of the excited state predicts that III or IV should be favored over any skewed form. Although this reversal of the bond orders in the excited state (singlet or triplet) would provide a driving force for attainment of a coplanar conformation regardless of opposing steric effects, Sidman and McClure[19] found that the vibrational frequencies of the C–C and C–O bonds did not change greatly in going from the ground state to the first excited singlet state in biacetyl. This contrasts with the results obtained for the formally analogous α,β-unsaturated aldehyde acrolein (V).[24] For this compound the energy barriers for rotation in the excited state are in good agreement with the simple molecular orbital prediction. The ground-state barriers are 8700 and 2270 cm^{-1} for the terminal and central C–C bonds, respectively, while in the excited singlet state the barriers are, respectively, 2700 and 5300 cm^{-1}.



III



IV



V

Experimental Section

The emission, excitation, and liquid nitrogen absorption measurements were made on an Aminco-Bowman spectrophotofluorometer with a phosphoroscope and transmission attachments. The spectrophotofluorometer was equipped with a 1P21 photomultiplier and a high pressure xenon lamp, as supplied by the manufacturer. The absorption measurements reported in Table I were recorded on a Perkin-Elmer 202 ultraviolet–visible spectrophotometer. All absorption and emission spectra were recorded using EPA (ethyl ether–isopentane–ethanol, 5:5:2 volume ratio) as solvent. The solvent was checked for emission each time a spectrum was recorded. No interference due to solvent was found at any time. The absorption spectra of biacetyl, 2,3-pentanedione, pivalil, bornanedione, and benzil were measured using the Aminco-Bowman SPF with a transmission attachment, both at room temperature and at 77°K. With the exception of bornanedione (*vide supra*), the long wavelength absorption maxima were the same at the two temperatures.

Bornanedione, benzil, and α-pyridil were purchased commercially and sublimed before use. Biacetyl, 2,3-pentanedione, 1,2-cycloheptanedione, 1,2-cyclodecanedione, 1-phenyl-1,2-propanedione, and α-furil were obtained commercially and used without further purification. Pivalil was prepared by the method of Leonard and Mader,[3] and purified by preparative gas chromatography. As used, the excitation spectra of all of the above diketones corresponded to the absorption spectra.

Acknowledgments. The authors are indebted to Lawrence D. Weis for technical assistance, and to the National Institutes of Health (Grant GM13592-01) and the Petroleum Research Fund of the American Chemical Society for generous financial support.

---

(22) C. Reid, *J. Chem. Phys.*, **21**, 1906 (1953).

(23) S. P. McGlynn and F. J. Smith in "Modern Quantum Chemistry," Part III, O. Sinanoglu, Ed., Academic Press Inc., New York, N. Y., 1965, p 67.

(24) J. C. D. Brand and D. G. Williamson, *Discussions Faraday Soc.*, **35**, 184 (1963).