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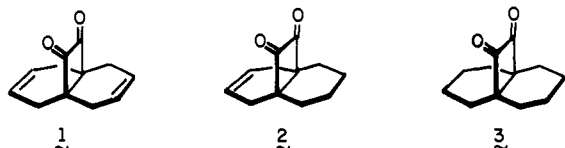
## Long-Range Electronic Transmission in Conformationally Rigid $\alpha$ -Diketones

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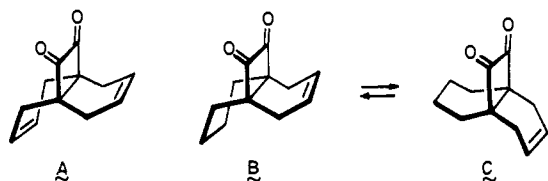
**Abstract:** The conformationally rigid  $\alpha$ -diketones **4-7** have been synthesized and their photoelectron (PE), absorption, and emission spectra recorded. Assignment of the first bands in the PE spectra is based upon correlation with related molecules and substantiated by MINDO/3 results. The first band ( $\pi^* \leftarrow n$ ) in the electronic spectra of **4-6** shows a hypsochromic shift through the series. This finding is explained in terms of interaction involving the  $\pi^*$  orbital of the  $C_2O_2$  fragment and the  $\pi$  orbital of the olefinic moiety in **4** and **5**. This interpretation is supported by CNDO/S calculations.

The visible spectra of the [4.4.2]propella-11,12-diones **1-3** were reported a decade ago to be characterized by most unusual features.<sup>4</sup> While **4** and **3** exhibit vastly different single long wavelength absorption maxima at 537.5 nm ( $\epsilon$  71.7) and 461 (73), respectively, dihydro derivative **2** shows two maxima at 460-464 and 532-535 nm. In the case of **2** and **3**, the first



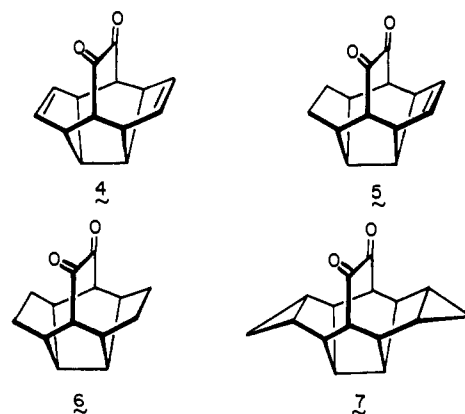
band is of Gaussian shape without vibrational fine structure. The first band in the electronic absorption spectrum of **1**, however, shows vibrational structure with the 0-0 progression as the most intense peak. Since this disclosure, considerable interest has developed in elucidating the manner by which  $\alpha$ -dicarbonyl systems find it possible to interact with proximate  $\pi$  bonds.

In a rationalization of their original findings, Bloomfield and Moser attributed these phenomena to "resonance stabilization of the excited state [involving] interspatial interaction between a double bond in the six-membered ring and the dione".<sup>4a</sup> The added suggestion was made that the appearance of the spectrum of **2** as a simple mixture of **1** and **3** results from adoption by **1** of conformation A and by **2** of the pair of interconverting conformations B and C. However, detailed MO calculations



caused this explanation to be later discarded and replaced by an assertion that through-bond interaction clearly predominates.<sup>4b</sup> A more recent detailed investigation of the electronic absorption and photoelectron spectra of **1-3** has brought to light the fact that the **1**-like absorption component of **2** disappears at 77 K, the residual band being essentially identical with that of **3**.<sup>5</sup> To explain these observations, different conformations of the six-membered rings and accompanying changes in the CO/CO dihedral angle were suggested.<sup>6</sup>

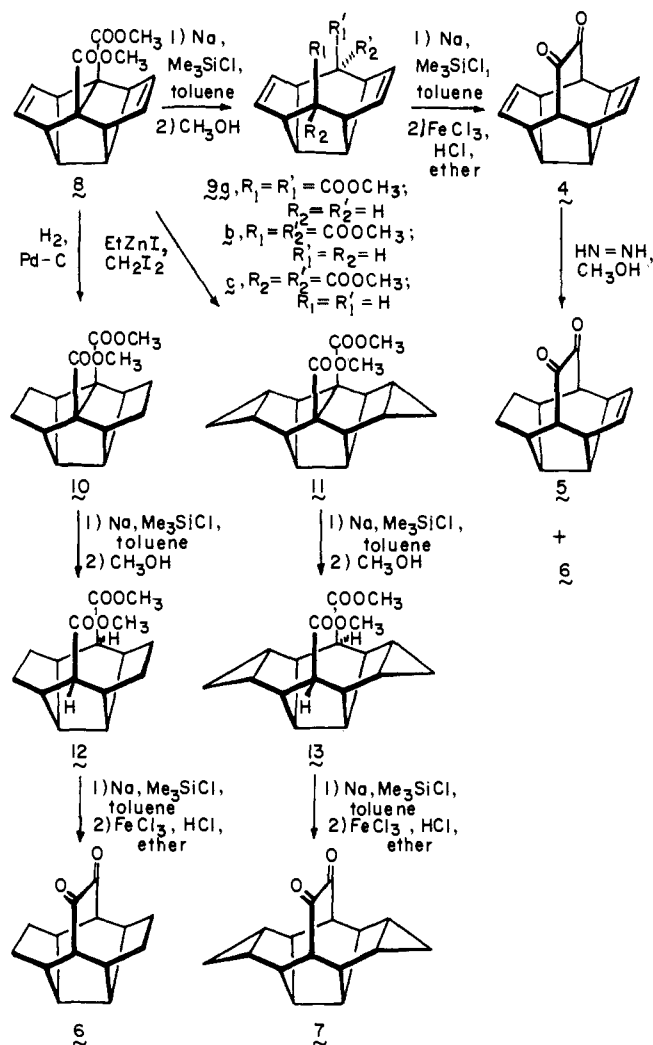
Because no adequate test of this interpretation has previously been devised, we were led to synthesize the  $\alpha$ -diketones **4-7** and to analyze their photoelectron (PE) and electronic



spectra. Because these molecules are highly rigid, the geometrical relationships of the double bonds (or cyclopropane rings) to the -COCO- moieties can be estimated with a high level of confidence. The major uncertainty prevailing in discussions to the present time is thereby eliminated.

**Synthetic Considerations.** The successful domino Diels-Alder cycloaddition of dimethyl acetylenedicarboxylate to

9,10-dihydrofulvalene has been described previously.<sup>7,8</sup> Insofar as product diester **8** is concerned, this multiple bonding scheme results in relatively efficient one-step construction of a carbocyclic frame closely related to that required in **4-7**. Reductive cleavage of the internal bond in **8** took place upon overnight heating in toluene with trimethylchlorosilane and dispersed sodium.<sup>9</sup> Kinetically controlled protonation of the bis ketene acetal so produced with methanol culminated in the production of a mixture of diesters (95%) consisting (<sup>1</sup>H NMR analysis) of **9a** (77%), **9b** (22%), and **9c** (1%) from which the pure endo,endo isomer could be isolated by fractional crystallization.<sup>10</sup> The C<sub>2v</sub> symmetry of **9a** follows from its <sup>1</sup>H (a single -OCH<sub>3</sub> absorption) and <sup>13</sup>C NMR spectra (six lines). Its sterically congested construction was made apparent by



equilibration with a catalytic amount of sodium methoxide in methanol at room temperature. Such treatment resulted in formation of a 1:4 mixture of **9b** and **9c**. Although the central bond in **8** can also be cleaved with sodium in liquid ammonia at -78 °C,<sup>11</sup> quenching of the resulting bisenolate with aqueous ammonium chloride solution did not lend itself to adequate stereochemical control of the protonation process. A mixture of **9a-c** was obtained containing roughly equal amounts of the three epimers.

The availability of pure **9a** permitted subsequent acyloin cyclization<sup>12</sup> and direct oxidation of the  $\alpha$ -hydroxy ketone with ferric chloride and hydrochloric acid in ether.<sup>13</sup> Pivotal diketone **4** was isolated in 65% yield. Controlled diimide reduction of **4** provided **5** and **6**.

This convenient methodology was subsequently applied to **10** and **11**, which were conveniently prepared by catalytic hydrogenation and Simmons-Smith cyclopropanation, re-

spectively, of **8**. Because it proved tedious to crystallize **12** from the mixture of diesters produced from the reductive cleavage of **10**, the preferred route to this intermediate consisted of hydrogenating **9a**. In contrast, the conversion of **11** to crystalline **13** proved highly efficacious.

**Photoelectron Spectra of 4-7.** The PE spectra of  $\alpha$ -diketones **4-7** are shown in Figure 1 and the measured vertical ionization potentials are compiled in Table I together with the results of molecular orbital calculations. Our interpretation of these data is based upon Koopmans' theorem<sup>14</sup>

$$-\epsilon_j = I_{V,j}$$

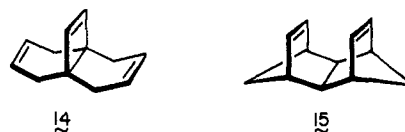
wherein the negative value of the orbital energy ( $\epsilon_j$ ) is construed to be equal to the vertical ionization potential ( $I_{V,j}$ ).

**Comparison with Related PE Spectra.** Correlation of our PE data with that of related molecules is possible under the present circumstances since interaction of the -COCO- moiety with the remainder of the individual molecules is small, at least as concerns the highest occupied MOs. The feasibility of such a comparative analysis is further substantiated by semiempirical calculations as discussed in the ensuing paragraph.

With reliance upon past experience,<sup>15,16</sup> a split between the two lone pair combinations

$$n_{\pm} = \frac{1}{2}(2p_{\pm} \pm 2p_2)$$

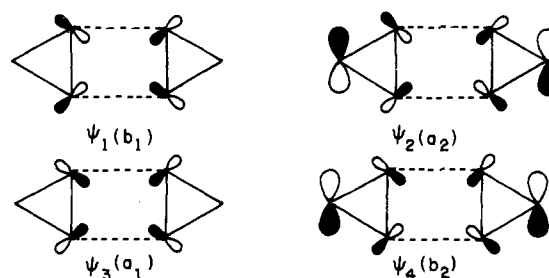
of about 1.5 eV with  $n_+$  above  $n_-$  is to be expected. From the ionization potential of norbornene (8.97 eV)<sup>17</sup> and the inductive effect of the C<sub>2</sub>O<sub>2</sub> unit (0.4-0.5 eV),<sup>15</sup> we estimate the  $\pi$  band to appear at approximately 9.5 eV. Considerable through-bond interaction<sup>18</sup> of the  $\pi$ -orbital electrons with the  $\sigma$  frame should be operative, however. Through-bond interaction across four  $\sigma$  bonds has previously been noted in [4.4.2]propella-3,8,11-triene (**14**)<sup>19</sup> and hydrocarbon diene **15**.<sup>20</sup> From these examples, we estimate a split between the  $\pi_-$



and  $\pi_+$  linear combinations (sketched below) of about 0.5-1.0 eV. Previous experience<sup>17,19,21</sup> has shown that the successive introduction of nonconjugated double bonds into a mono- or polycyclic monoene shifts the center of gravity  $\bar{\epsilon}(\pi)$  toward lower energies by -0.1 to -0.2 eV per added double bond. On this basis, the bands in **4** due to ionization from  $\pi_-$  and  $\pi_+$  should appear between 9 and 10 eV.



For **7**, the assignment is difficult owing to the strong overlap of bands in the region from 9.6 eV on. However, it does appear very likely that the orbital energies of the four linear combinations ( $\psi_1$ - $\psi_4$ ) of the Walsh orbitals (top views are illustrated below) fall into this region together with the  $n_-$  combination.



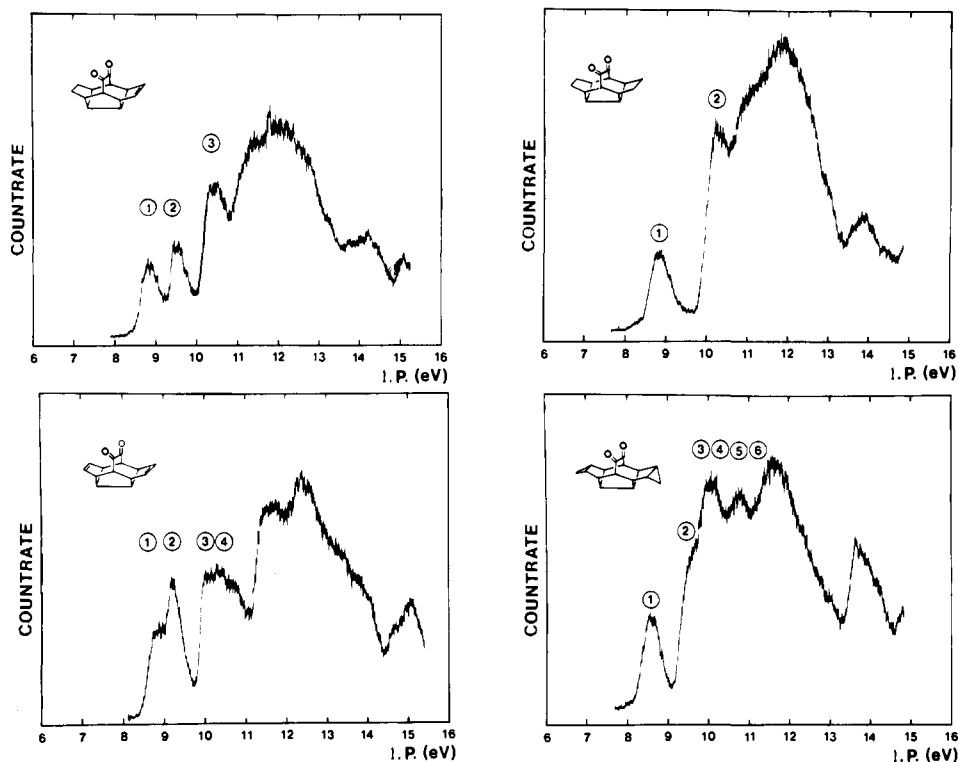


Figure 1. PE spectra of 4-7 between 8 and 16 eV.

Table I. Comparison between Measured Vertical Ionization Potentials,  $I_{V,J}$ , of 4-7 and Calculated Orbital Energies (eV)

compd	$H_f$ kcal/mol	band	$I_{V,J}$	assignment	$-\epsilon_j(\text{MINDO}/3)$	$-\epsilon_j(\text{CNDO}/S)$
4 ( $C_{2v}$ )	88.41	①	8.85	$a_1(n_+)$	8.69	9.28
		②	9.15	$b_1(\pi_-)$	9.25	9.42
		③	10.0	$a_1(\pi_+)$	9.61	9.86
		④	10.3	$b_2(n_-)$	10.41	11.43
5 ( $C_s$ )	53.62	①	8.80	$a'(n_+)$	8.77	9.33
		②	9.45	$a'(\pi)$	9.51	9.72
		③	10.4	$a''(n_-)$	10.37	11.39
6 ( $C_{2v}$ )	19.96	①	8.82	$a_1(n_+)$	8.85	9.43
		②	10.26	$b_2(n_-)$	9.87	11.32
7 ( $C_{2v}$ )	87.33	①	8.6	$a_1(n_+)$	8.70	9.37
		②	9.6	$b_1(\psi_1)$	9.56	10.55
		③	10.0	$a_2(\psi_2)$	9.75	11.00
		④	10.14	$a_1(\psi_3)$	9.99	11.14
		⑤	10.7	$b_2(n_-)$	10.23	11.32
		⑥	10.7	$b_2(\psi_4)$	10.74	12.00

**MINDO/3 Calculations.** Dewar's MINDO/3 method<sup>22</sup> has proven to be extremely reliable in predicting the orbital energies of  $\alpha$ -dicarbonyl groups contained in a hydrocarbon framework.<sup>15</sup> Because the precise structures of 4-7 are not known, their geometries were optimized within the MINDO/3 scheme. For this purpose, a modified Fletcher-Powell search procedure<sup>23</sup> was used. The heats of formation so obtained are given in Table I. To reduce the large number of variables,  $C_{2v}$  symmetry was assumed for 4, 6, and 7, while 5 was assigned  $C_s$  symmetry. The resultant agreement between the MINDO/3 calculations and experiment proved excellent (Table I).

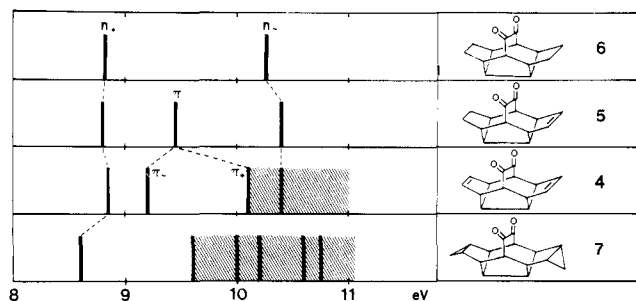
The first bands in the PE spectra of 4-7 have been correlated in Figure 2. From this drawing, two observations are noteworthy: (1) the constancy of the split between  $n_-$  and  $n_+$  in all compounds and (2) the relatively large split between  $\pi_-$  and  $\pi_+$  in the case of 4. According to our calculations, this split is due to a strong through-bond interaction between the  $\pi_-$  linear combination and the  $\sigma$  frame as discussed above.

**Electronic Spectra.** The relatively weak first absorption band

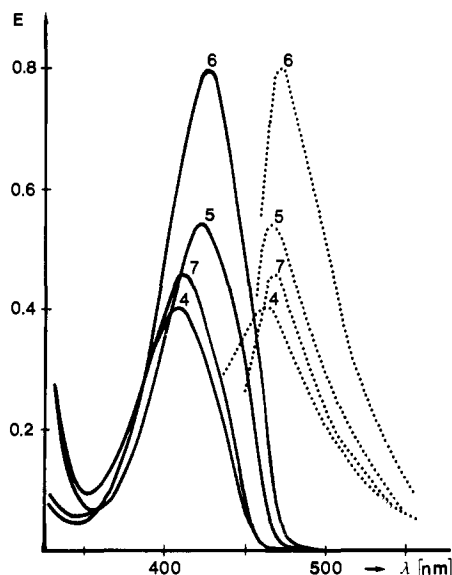
(A) of 4-7 is, of course, responsible for the yellow color of these compounds. A comparison of these bands is made in Figure 3 together with the measured emission spectra. The experimentally determined absorption data for the region between 230 and 450 nm are contrasted in Table II with the results of a CNDO/S calculation.<sup>24</sup> The geometrical parameters taken for these calculations were those derived from the geometry minimization mentioned above. In contrast to the first band in the electronic absorption spectra of 1-3, a hypsochromic shift is observed in going from the hydrogenated species 6 to its doubly unsaturated counterpart 4. In all four cases (4-7), a Gaussian shape of the first absorption and emission band without fine structure is found.

In Table III are listed the shifts between the maxima of the first absorption and emission bands. Compared with the shifts observed for other less rigid  $\alpha$ -dicarbonyls,<sup>25</sup> the changes found are very small.

The calculations assign the first transition as one proceeding from the HOMO (the  $n_+$  linear combination defined above) to the LUMO ( $\pi_+$ ). The latter arises from linear combination



**Figure 2.** Correlation between the first bands of the PE spectra of 4-7 based on MINDO/3 calculations. Strongly overlapping bands are indicated by the shaded areas.



**Figure 3.** Comparison between the first bands in the electronic absorption (—) and uncorrected emission (.....) spectra of 4-7 in methylene chloride.

of the two  $\pi^*$  orbitals ( $\pi_1^*$  and  $\pi_2^*$ ) located at the carbonyl groups.

$$\pi_{\pm}^*(\text{CO}) = 1/\sqrt{2} (\pi_1^*(\text{CO}) \pm \pi_2^*(\text{CO}))$$

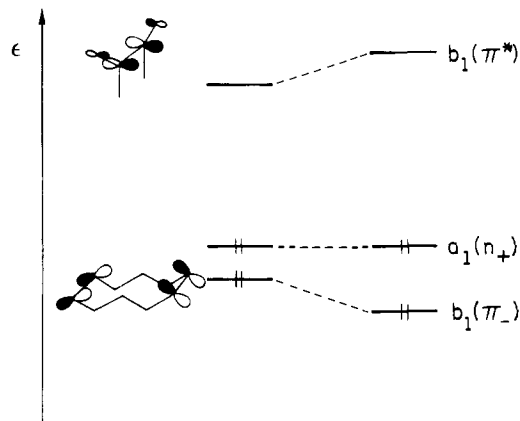
This assignment is corroborated by the relatively low intensity (see Table II) of the first band and the hypsochromic shift observed upon changing from the aprotic solvent methylene chloride to ethanol.

At higher energies, at least two more bands (B and C) are observed for 4 and one additional band (B) for 5 (Table II). These are assigned to a mixture of several configurations involving  $\pi^*(\text{CO}) \leftarrow \pi$  and  $\pi^*(\text{CC}) \leftarrow \pi$  transitions.

To rationalize the bathochromic shift noted in going from 4 to 6, several points should be considered: (1) the effect of different CO/CO dihedral angles in the ground state,  $\theta_g$ , and first excited state,  $\theta_{ex}$ ; (2) the ionization potential corresponding to the  $n_+$  combination (HOMO); and (3) a spatial interaction between the  $\pi_1^*$  linear combination of the  $\text{C}_2\text{O}_2$  moiety and  $\pi$  of the olefinic moieties in 4 and 5 or the Walsh combination  $\psi_1(b_1)$  in 7.

Extensive studies on the electronic spectra of  $\psi$ -dicarbonyls<sup>25</sup> have shown that  $\theta_{ex}$  is about  $0^\circ$  and that the difference  $\theta = |\theta_g - \theta_{ex}|$  can vary considerably. A good estimate for this change can be gained by measuring the energy difference between the maximum of the first bands in the absorption and emission spectra. In our case, only small differences were noted in the series 4-7 (see Figure 3 and Table III).

Looking at the ionization potentials of the first bands in the



**Figure 4.** Comparison of the orbital energies for 4 without (left) and with (right)  $\pi_+^*-\pi_-$  interaction.

PE spectra of 4-6 (Table I), we find essentially no change. This eliminates point (2) in the list above. What remains to be considered is a spatial interaction between  $b_1(\pi_-)$  of the olefinic part of 4 and  $b_1(\pi_+^*)$  of the  $\text{C}_2\text{O}_2$  group. According to the calculations, there is a spatial interaction between these two orbitals which leads to an energy separation between  $n_+$  and  $\pi_+^*$ . Suitable comparison with a model in which this is not possible, e.g., 6, nicely illustrates these features (see Figure 4).

## Discussion

This study of the conformationally rigid  $\alpha$ -diketones 4-6 has permitted unequivocal assignment to be made to the PE bands between 8 and 11 eV. Importantly, there is found to exist a strikingly close similarity to the PE spectra of 1-3.<sup>6</sup>

The first band in the electronic spectra of 4-6 shows a trend opposite to that found for 1-3, namely, a bathochromic shift in the first series but a hypsochromic shift in the latter. In addition to this, the shapes of the first bands in 1-3 show differences as described in the introduction. This latter observation strongly suggests different values for  $\theta$  depending on the rigidity of the six-membered rings. In the most rigid system, 1, the change in  $\theta$  is minute, therefore the  $0 \leftarrow 0$  component is the most intensive peak. In 2 and 3, where hydrogenation renders more flexibility to the whole system,  $\theta$  is larger. This effect will cause a hypsochromic shift which apparently overrides the through-space effect. An additional effect which might play a role in the electronic spectra of the series 1-3 is an anti arrangement of the  $\pi$  bond(s) in 1 and 2 relative to the  $\text{C}_2\text{O}_2$  fragment as in E and C, respectively. This presumption accords with CNDO/S calculations on D and E. Thus, values



of 427 and 444 nm are predicted for the first band of D and E.

## Experimental Section

Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer and  $^{13}\text{C}$  spectra were recorded on a Bruker HX-90 instrument. Infrared spectra were determined on a Perkin-Elmer Model 467 spectrophotometer while mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. The electronic spectra were recorded (Cary 15) at room temperature in cyclohexane, methylene chloride, and ethanol between 220 and 500 nm. The emission spectra were measured (Hitachi Perkin-

Table II. Measured and Calculated Electronic Absorption Spectra of 4-7

compd	observed			$\lambda$ , nm	calculated predominant configuration
	band	$\lambda$ , nm	$\log \epsilon_{\max}$		
4	A	408.5 <sup>a</sup>	1.20	405.4	$\pi^*(\text{CO}) \leftarrow n_+$ (74%); $\pi^* \leftarrow n_+$ (26%)
		403.7 <sup>b</sup>	1.18		
	B	271.5 <sup>c</sup>	3.14	270.9	$\pi^*(\text{CO}) \leftarrow n_+$ (26%); $\pi^* \leftarrow n_+$ (74%)
5	A	228.5 <sup>c</sup>	3.99	212.4	$\pi^*(\text{CO}) \leftarrow \pi_-(\text{C}=\text{C})$ (100%)
		421.0 <sup>a</sup>	1.34		
6	B	417.6 <sup>b</sup>	1.33	306.1	$\pi^*(\text{CO}) \leftarrow n_+$ (40%); $\pi^*(\text{CO}) \leftarrow n_-$ (44%)
		255.7 <sup>c</sup>	3.54		
	A	427.2 <sup>a</sup>	1.49	456.7	$\pi^*(\text{CO}) \leftarrow n_+$ (94%)
7	A	424.2 <sup>b</sup>	1.48	456.0	$\pi^*(\text{CO}) \leftarrow n_+$ (90%)
		412.0 <sup>a</sup>	1.23		
	B	407.4 <sup>b</sup>	1.22	302.0	$\pi^*(\text{CO}) \leftarrow n_+$ (58%); $\pi^*(\text{CO}) \leftarrow n_-$ (41%)
		230.0 <sup>c</sup>	3.61		

<sup>a</sup> Methylene chloride. <sup>b</sup> Ethanol. <sup>c</sup> Cyclohexane.

Table III. Emission Data of Compounds 4-7 (CH<sub>2</sub>Cl<sub>2</sub> solution)<sup>a</sup>

compd	$\lambda_{\max}$ , nm	$\bar{\nu}_{\max}$ , cm <sup>-1</sup>	$\bar{\nu}_{\max}^{\text{emiss}} - \bar{\nu}_{\max}^{\text{abs}}$ , cm <sup>-1</sup>
4	464.0	21 552	2928
5	465.5	21 482	2271
6	473.0	21 142	2267
7	470.0	21 277	2995

<sup>a</sup> The data are uncorrected.

Elmer MPF 3) at room temperature in methylene chloride solution. The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin-Elmer Ltds., Beaconsfield, Ill.) equipped with a heated probe. The light source was a He (I $\alpha$ ) lamp. All samples had to be heated: 4 (100 °C), 5 (100 °C), 6 (90 °C), and 7 (130 °C). The spectra were calibrated with argon and resolution of about 20 meV on the argon line was obtained. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

For the MINDO/3 calculations, we made use of a program efficiently modified by Dr. P. Bischof. For the CNDO/S calculations, the program published by QCPE, Indiana University, was employed. All calculations were performed on an IBM 370/168 computer precision versions of the computer programs.

**Reductive Cleavage of 8.** In a dry 250-mL three-necked flask equipped with condenser, Hershberg stirrer, and nitrogen inlet was heated freshly cut sodium (3.4 g, 0.148 g-atom) in 90 mL of dry toluene with rapid stirring under nitrogen until a fine dispersion was formed. Trimethylchlorosilane (20 mL, 0.157 mol) was introduced via syringe from the top of the condenser. A solution of diester 8 (1.028 g, 3.77 mmol) in 10 mL of dry toluene was added dropwise. After being stirred at the reflux temperature for 13.5 h, the dark mixture was filtered through Celite. Excess trimethylchlorosilane was removed by concentration of the filtrate under reduced pressure. The concentrate was then added dropwise to 100 mL of dry methanol with stirring under nitrogen. After dilution of the methanolic solution with 500 mL of water, the layers were separated. The aqueous layer was extracted with pentane (3  $\times$  100 mL) after which the combined organic layers were washed with water (3  $\times$  200 mL) and dried. Concentration yielded a yellow oil which was chromatographed on silica gel. Hexane elution removed silylated products while 20% ether in hexane afforded 0.977 g (95%) of the diester mixture, which consisted of 9a (77%), 9b (22%), and 9c (1%) (<sup>1</sup>H NMR analysis). Repeated recrystallization from hexane afforded pure 9a: mp 84-84.5 °C;  $\nu_{\max}$  (KBr) 1738 and 1195 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 5.66 (s, 4 H), 3.70 (s, 6 H), and 2.91-3.64 (m, 8 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 173.19, 134.08, 53.09, 51.52, 51.31, and 49.04; *m/e* calcd 274.1205, obsd 274.1210.

Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>: C, 70.05; H, 6.61. Found: C, 70.10; H, 6.78.

**Base-Catalyzed Equilibration of 9a.** A crude mixture of diesters prepared as described above (0.62 g, 2.26 mmol) was treated with a catalytic amount of sodium methoxide in 30 mL of dry methanol at room temperature for 4.5 days under nitrogen. After the addition of 10 mL of saturated aqueous ammonium chloride, the reaction mixture was diluted with 300 mL of water and extracted with ether (3  $\times$  100 mL). The combined ethereal layers were washed with water (1  $\times$  200

mL) and brine (1  $\times$  200 mL) prior to drying. Removal of the solvent yielded a yellow oil which was chromatographed on silica gel. The diester mixture (0.58 g) was recovered in 94% yield from the column upon elution with 40% ether in hexane. The composition was determined to be 80% of 9c and 20% of 9b by <sup>1</sup>H NMR analysis. Repeated recrystallization from hexane afforded pure 9c: mp 75.5-77 °C;  $\nu_{\max}$  (KBr) 1738, 1175, and 740 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 5.37 (s, 4 H), 3.68 (s, 6 H), 3.33-3.68 (m, 6 H), and 2.91 (s, 2 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 176.37, 135.15, 56.08, 54.55, 52.66, and 51.80; *m/e* calcd 274.1205, obsd 274.1210.

Anal. Calcd for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>: C, 70.05; H, 6.61. Found: C, 69.96; H, 6.71.

Partial <sup>1</sup>H NMR data for endo,exo isomer 9b ( $\delta$ , CDCl<sub>3</sub>) 5.45 (AB q, *J*<sub>AB</sub> = 5.5 Hz,  $\Delta V_{AB}$  = 15.6 Hz, 4 H).

**Catalytic Hydrogenation of 8.** A solution of 8 (1.00 g, 3.67 mmol) in 60 mL of ethyl acetate containing 10% palladium on charcoal was hydrogenated in a Parr apparatus at 50 psig for 16 h. The catalyst was removed by filtration through a pad of Celite and rinsed with 50 mL of methylene chloride. Evaporation of the combined filtrates gave 1.08 g of colorless solid which was recrystallized from hexane to afford 0.93 g (92%) of 10 as white needles: mp 139-139.5 °C;  $\nu_{\max}$  (KBr) 1720 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 3.67 (s, 6 H), 2.47 (m, 6 H), and 1.68 (m, 8 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 172.33, 60.37, 58.00, 51.15, 47.53, and 22.55; *m/e* calcd 276.1361, obsd 276.1366.

Anal. Calcd for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>: C, 69.54; H, 7.30. Found: C, 69.36; H, 7.20.

**Cyclopropanation of 8.** A 1 M solution of ethylzinc iodide in ether (27.0 mL, 27.0 mmol) contained in a 100-mL three-necked flask equipped with nitrogen inlet, condenser, rubber septum, and magnetic stirring bar was treated via syringe with 2.2 mL (27.0 mmol) of methylene iodide. The resulting solution was heated at reflux for 30 min prior to dropwise addition of 8 (500 mg, 1.84 mmol) in dry ether (5 mL) at room temperature. After being heated at the reflux temperature for 18 h, the reaction mixture was poured into cold saturated ammonium chloride solution (70 mL). The ether phase was separated and the aqueous layer extracted with ether (40 mL). The combined ether solutions were washed with saturated ammonium chloride solution, dried, and concentrated to give 710 mg of oily yellow solid. Chromatography on silica gel (elution with 20% ether in hexane) afforded 523 mg of white solid which was recrystallized from hexane. There resulted 395 mg (72%) of 11: mp 123-123.5 °C;  $\nu_{\max}$  (KBr) 1741 and 1722 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 3.48 (s, 6 H), 2.43 (m, 2 H), 1.57 (m, 2 H), 1.25-0.88 (br m, 4 H), and 0.17 to -0.33 (br m, 4 H); <sup>13</sup>C NMR (ppm, CDCl<sub>3</sub>) 172.40, 64.52, 57.34, 51.22, 35.34, 10.49, and 2.38; *m/e* calcd 300.1361, obsd 300.1367.

Anal. Calcd for C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>: C, 71.98; H, 6.71. Found: C, 71.84; H, 6.62.

**Reductive Cleavage of 10.** A 250-mg (0.911 mmol) sample of 10 was treated as above with sodium dispersion (821 mg, 35.7 mg-atoms) and trimethylchlorosilane (6.0 mL, 47.3 mmol) in anhydrous toluene (25 mL). After 8 h at the reflux temperature, the excess sodium was removed by filtration through a Celite pad, the filtrate was concentrated in vacuo, and the residue was added as a solution (5 mL) in dry toluene to methanol. The resultant yellow oil (352 mg) was chromatographed on silica gel (elution with 20% ether in hexane) to give 157 mg (62%) of 12 as colorless crystals: mp 94.5-95.5 °C (from hexane);  $\nu_{\max}$  (KBr) 1734 and 1190 cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ , CDCl<sub>3</sub>) 3.67 (s, 6 H),

3.47–2.53 (br m, 8 H), and 2.10–1.58 (br m, 8 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 173.95, 56.61, 54.47, 51.02, 46.36, and 30.49;  $m/e$  calcd 278.1518, obsd 278.1524.

Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_4$ : C, 69.04; H, 7.97. Found: C, 69.11; H, 7.94.

The same diester (12) was prepared by catalytic reduction of 9a (50 mg, 0.182 mmol) in ethyl acetate (5 mL) containing 10% palladium on carbon (20 mg) at 50 psig of hydrogen. Removal of the catalyst and concentration of the filtrate yielded 49.7 mg (98%) of 12.

**Reductive Cleavage of 12.** Treatment of 12 (200 mg, 0.67 mmol) with sodium dispersion (603 mg, 26.2 mg-atoms) and trimethylchlorosilane (4.5 mL, 34.8 mmol) in dry toluene (20 mL) in the pre-described manner afforded after 7 h a light yellow oil (284 mg) which was chromatographed on silica gel. Elution with 20% ether in hexane afforded 181 mg (89.6%) of 13 as white crystals: mp 128–129 °C (from hexane);  $\nu_{\text{max}}$  (KBr) 1735  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 3.63 (s, 6 H), 3.13–2.35 (br m, 8 H), 1.58–1.22 (m, 4 H), 1.02–0.55 (br m, 2 H), and –0.12 to –0.42 (m, 2 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 173.67, 60.26, 55.11, 51.42, 50.55, 24.53, and 17.73;  $m/e$  calcd 302.1518, obsd 302.1522.

Anal. Calcd for  $\text{C}_{18}\text{H}_{22}\text{O}_4$ : C, 71.50; H, 7.34. Found: C, 71.51; H, 7.43.

**Acyloin Cyclization of 9a.** To a dispersion of sodium (3.28 g, 143 mg-atoms) in dry toluene (100 mL) was added trimethylchlorosilane (20 mL, 154 mmol) followed dropwise by 9a (1.0 g, 3.64 mmol) in 20 mL of the same solvent. The resultant mixture was heated at reflux under nitrogen for 13 h, freed of sodium by filtration through a Celite pad (toluene rinse), and concentrated under reduced pressure. The residue dissolved in dry toluene (25 mL) was added dropwise under nitrogen to a stirred solution of anhydrous ferric chloride (1.78 g, 11.0 mmol) in 50 mL of dry ether containing 10 drops of concentrated hydrochloric acid. The dark green mixture was gently refluxed for 1 h, cooled, and treated with 100 mL of saturated aqueous ammonium sulfate solution. The layers were separated and the aqueous ammonium sulfate solution. The layers were separated and the aqueous phase was extracted with methylene chloride (3  $\times$  100 mL). The combined organic solutions were washed with dilute sodium bicarbonate solution (80 mL) and brine (80 mL) prior to drying and solvent removal. The residual yellow, crystalline solid was purified by silica gel chromatography (elution with 20% ether in hexane) and 4 was isolated as yellow needles (0.50 g, 65%): mp 246 °C dec (from ethyl acetate–hexane);  $\nu_{\text{max}}$  (KBr) 1720, 1710, 1696, and 1691  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.65 (d,  $J = 1$  Hz, 4 H), 3.83–3.23 (br m, 6 H), and 3.13–2.70 (br m, 2 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 195.96, 132.36, 57.29, 56.38, and 51.34;  $m/e$  calcd 212.0837, obsd 212.0840.

Anal. Calcd for  $\text{C}_{14}\text{H}_{12}\text{O}_2$ : C, 79.22; H, 5.70. Found: C, 79.24; H, 5.94.

**Acyloin Cyclization of 12.** Reaction of 12 (100 mg, 0.36 mmol) with sodium dispersion (324 mg, 14.1 mg-atoms) and trimethylchlorosilane (2.28 mL, 18.0 mmol) in dry toluene (14 mL) for 13.5 h and subsequent oxidation with anhydrous ferric chloride (175 mg, 1.08 mmol) in dry ether (5 mL) containing 6 drops of concentrated hydrochloric acid as described above gave 150 mg of oily, yellow solid. Chromatography on silica gel (elution with 20% ether in hexane) afforded 42 mg (55%) of 6 as yellow needles: mp 181–182.5 °C (from hexane);  $\nu_{\text{max}}$  (KBr) 1701  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 2.98 (br m, 8 H) and 2.17–1.37 (br m, 8 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 201.11, 60.50, 56.20, 51.89, and 28.34;  $m/e$  calcd 216.1150, obsd 216.1154.

Anal. Calcd for  $\text{C}_{14}\text{H}_{16}\text{O}_2$ : C, 77.74; H, 7.46. Found: C, 77.62; H, 7.56.

**Diimide Reduction of 4.** A solution of 4 (400 mg, 1.89 mmol) in 40 mL of dry methanol containing potassium azodicarboxylate (399 mg, 2.05 mmol) was treated dropwise under nitrogen at –78 °C with glacial acetic acid (400  $\mu\text{L}$ , 7.00 mmol). After completion of the addition, the mixture was stirred for 30 min at –78 °C and for 3 h at room temperature. Additional potassium azodicarboxylate (160 mg, 0.82 mmol) and glacial acetic acid (6 drops) were added at 0 °C and the mixture was maintained at this temperature for 12 h before dilution with water (50 mL) and extraction with methylene chloride (2  $\times$  50 mL). The combined organic layers were washed with 10% aqueous sodium bicarbonate solution (50 mL) and water (50 mL) prior to drying and concentration. Preparative thin layer chromatography of the residue (457 mg) on silica gel (four elutions with 30%

ethyl acetate in hexane) afforded 34.4 mg of 6 ( $R_f$  0.23), 40.3 mg of recovered 4 ( $R_f$  0.39), and 104 mg (26%) of the desired 5, yellow plates: mp 182.5–184 °C (from hexane);  $\nu_{\text{max}}$  (KBr) 2941, 1720, 1710, 1704, and 1685  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 5.64 (d,  $J = 1$  Hz, 2 H), 3.51 (m, 2 H), 3.09 (m, 6 H), and 2.38–1.13 (br m, 4 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 197.79, 130.89, 58.50, 57.63, 55.68, 53.99, 53.11, and 27.09;  $m/e$  calcd 214.0994, obsd 214.0997.

Anal. Calcd for  $\text{C}_{14}\text{H}_{14}\text{O}_2$ : C, 78.48; H, 6.58. Found: C, 78.79; H, 6.78.

**Acyloin Cyclization of 13.** Reaction of 13 (100 mg, 0.33 mmol) with sodium dispersion (299 mg, 13.0 mg-atoms) and trimethylchlorosilane (2.11 mL, 16.6 mmol) in dry toluene (14 mL) for 12 h and subsequent oxidation with anhydrous ferric chloride (161 mg, 0.993 mmol) in dry ether (5 mL) containing 6 drops of concentrated hydrochloric acid as described above gave 131 mg of crude product. Chromatography on silica gel (elution with 20–40% ether in hexane) gave 7 (56 mg, 70%) as yellow crystals: mp 260.5–262 °C (from ethyl acetate);  $\nu_{\text{max}}$  (KBr) 1720 and 1703  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ) 3.35–2.60 (br m, 8 H), 1.25–0.95 (m, 4 H), and 0.65 to –0.02 (m, 4 H);  $^{13}\text{C}$  NMR (ppm,  $\text{CDCl}_3$ ) 198.14, 60.08, 52.13, 48.97, 19.12, and 10.01;  $m/e$  calcd 240.1150, obsd 240.1155.

Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_2$ : C, 79.97; H, 6.71. Found: C, 79.79; H, 6.75.

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## References and Notes

- (1) Technische Hochschule Darmstadt.
- (2) The Ohio State University.
- (3) Dissertation Fellow, 1977–1978.
- (4) (a) J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.*, **90**, 5625 (1968); (b) S. C. Neely, R. Fink, D. Van der Helm, and J. J. Bloomfield, *ibid.*, **93**, 4903 (1971).
- (5) D. Dougherty, J. J. Bloomfield, G. R. Newkome, J. F. Arnett, and S. P. McGlynn, *J. Phys. Chem.*, **80**, 2212 (1976).
- (6) The crystal structure of 1 has been determined and the two six-membered rings shown to adopt boat conformations folded toward the diketone as in D: R. Fink, D. Van der Helm, and S. C. Neely, *Acta Crystallogr., Sect. B*, **31**, 1299 (1975).
- (7) L. A. Paquette and M. J. Wyratt, *J. Am. Chem. Soc.*, **96**, 4671 (1974).
- (8) D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropoulos, and E. Hedaya, *J. Am. Chem. Soc.*, **98**, 4673 (1974).
- (9) J. J. Bloomfield, R. A. Martin, and J. M. Nelke, *J. Chem. Soc., Chem. Commun.*, 96 (1972).
- (10) M. J. Wyratt, Ph.D. Thesis, The Ohio State University, 1976.
- (11) P. G. Gassman and X. Creary, *J. Chem. Soc., Chem. Commun.*, 1214 (1972).
- (12) J. J. Bloomfield, D. C. Owsley, and J. M. Nelke, *Org. React.*, **23**, 259 (1976).
- (13) G. E. Gream and S. Worthley, *Tetrahedron Lett.*, 3319 (1968).
- (14) T. Koopmans, *Physica (Utrecht)*, **1**, 104 (1934).
- (15) R. Gleiter, R. Bartetzko, P. Hofmann, and H. D. Scharf, *Angew. Chem.*, **89**, 414 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 400 (1977); R. Gleiter, P. Schang, and G. Seitz, *Chem. Phys. Lett.*, in press; P. Schang, R. Gleiter, and A. Ricker, *Ber. Bunsenges. Phys. Chem.*, in press.
- (16) D. O. Cowan, R. Gleiter, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem.*, **83**, 405 (1971); *Angew. Chem., Int. Ed. Engl.*, **10**, 401 (1971).
- (17) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).
- (18) R. Hoffman, *Acc. Chem. Res.*, **4**, 1 (1971); R. Gleiter, *Angew. Chem.*, **86**, 770 (1974); *Angew. Chem., Int. Ed. Engl.*, **13**, 696 (1974), and references cited therein.
- (19) R. Gleiter, E. Heilbronner, L. A. Paquette, G. L. Thompson, and R. E. Wingard, Jr., *Tetrahedron*, **29**, 565 (1973).
- (20) H.-D. Martin and R. Schwesinger, *Chem. Ber.*, **107**, 3143 (1974).
- (21) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta*, **53**, 1645 (1970); C. Batick, P. Bischof, and E. Heilbronner, *J. Electron Spectrosc. Relat. Phenom.*, **1**, 333 (1972).
- (22) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285 (1975).
- (23) R. Fletcher and M. J. D. Powell, *Comput. J.*, **6**, 163 (1963).
- (24) H. H. Jaffé, *Acc. Chem. Res.*, **2**, 136 (1969) and references cited therein.
- (25) J. F. Arnett, G. Newkome, W. L. Mattice, and S. P. McGlynn, *J. Am. Chem. Soc.*, **98**, 4385 (1974); J. F. Arnett and S. P. McGlynn, *J. Phys. Chem.*, **79**, 626 (1975).