J. Am. Chem. Soc. **1983**, *105*, 145–146

to complete the assignments for the six pyrimidine imino hydrogens in *E. coli* tRNA$_f^{Met}$ seen between 11 and 15 ppm.[13] The power of the method is further illustrated by the discovery of the temperature-sensitive resonance for U27-A43. At the lower temperatures needed to observe the peak, all of the ^{1}H signals are significantly broader, and it would have been difficult to detect the appearance of the new signal at 14 °C without the difference experiment. The U27-A43 resonance accounts for one of the "missing" peaks in the 35 °C spectrum.[2]

Acknowledgment. We thank Professor Redfield for informing us about his NOE experiments and the National Science Foundation for support of this research by Grants PCM 79-16861 (to C.D.P.) and CHE 78-18581 (to the regional NMR facility at Colorado State University).

Registry No. Uridine, 58-96-8; 4-thiouridine, 13957-31-8; ribothymidine, 1463-10-1; pseudouridine, 1445-07-4; adenosine, 58-61-7; guanosine, 118-00-3.

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(13) The technique should be generally useful for detection of ^{1}H resonances and for chemical shift correlation in biopolymers labeled with NMR-active isotopes.

Circular Polarization of Luminescence as a Probe for Intramolecular $^1n\pi^*$ Energy Transfer in *meso*-Diketones

P. H. Schippers and H. P. J. M. Dekkers*

Gorlaeus Laboratories, University of Leiden
2300 RA Leiden, The Netherlands

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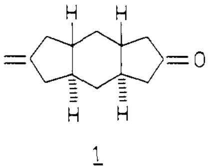
When a racemic mixture is excited with circularly polarized light, the degree of circular polarization in the luminescence (CPL) provides information on the rate of racemization in the excited state.[1,2] It appears, however, that the CPL technique can also be used to study intramolecular excitation energy transfer.

We here report measurements on aliphatic diketones that contain two remote carbonyl chromophores of opposite chirality and thus are, in the ground state, meso structures (*RS*). In the $^1n\pi^*$ state they may occur in two enantiomeric forms, R^*S and RS^*, provided the excitation energy remains localized at a carbonyl group. If the excited state is formed by irradiation with circularly polarized light, the concentrations of R^*S and RS^* are unequal, and the fluorescence will to some extent be circularly polarized. In complete analogy to the case of racemates,[2,3] the observed circular anisotropy equals $G_L = {}^1/_2 g_a g_e$, where the index L denotes the (left) handedness of the excitation light and g_a (g_e) the dissymmetry factor in absorption (emission) of the *R* and *S* carbonyl moieties. Irradiation with *R* light has the opposite effect: $G_R = -G_L$. So in the absence of energy transfer, the differential circular anisotropy $G_L - G_R$ equals $g_a g_e$. When during the fluorescence lifetime τ_F energy transfer (rate k_{ET}) occurs, a lower anisotropy will be observed, viz.

$$(G_L - G_R)_{obsd} = g_a g_e (2k_{ET}\tau_F + 1)^{-1}$$

Provided $g_a g_e$ is known, the observed differential polarization directly measures k_{ET} relative to τ_F.

We have studied the effect of the 1,7-diketone (1*S*,3*R*,7*R*,9*S*)-tricyclo[7.3.0.0^{3,7}]dodecane-5,11-dione (**1**)[4] and



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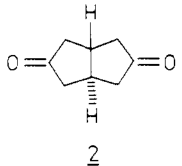
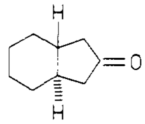


2



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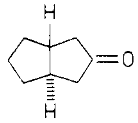

4

the 1,5-diketone *trans*-bicyclo[3.3.0]octane-3,7-dione (**2**).[5] The absorption spectra of **1** and **2** essentially are equal in shape and twice as intense as the spectra of the relevant monoketones **3** and **4**, respectively.[6] Also the fluorescence spectra of **1** and **2** closely resemble those of **3** and **4**, respectively.[6] Apparently in **1** and **2** the local $^1n\pi^*$ states are only very weakly coupled, justifying a description of absorption and emission in terms of local transitions.[7] Like in **3** and **4**, the carbonyl groups in **1** and **2** are contained in chirally twisted cyclopentane rings. Therefore, one expects that their g_a and g_e values equal those of **3** and **4** to a good approximation. It is known from experiment that the dissymmetry factors of **3**[8,9] and **4**[10,11] are large and virtually equal ($g_a \simeq 0.2$ in the long wavelength part of the n → π* absorption band and $g_e \simeq 0.03$ in the short wavelength part of the fluorescence band).

When exciting at 310 nm and collecting the fluorescence at 400 nm, we observed[12] for **1** the large differential polarization $G_L - G_R = (58 \pm 3) \times 10^{-4}$, whereas for **2** it proved to be zero: $G_L - G_R = (0 \pm 1) \times 10^{-4}$. The quantitative correspondence of $G_L - G_R$ of **1** with $g_a g_e$ of **3** (better than 95% as found from the experimental error in $G_L - G_R$) implies that $k_{ET} \lesssim 1 \times 10^7$ s^{-1} (calculated with $\tau_F = 2$ ns, the value found[13] for **3**).[14] On the other hand the complete disappearance (>98%) of the differential

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(1) Dekkers, H. P. J. M.; Emeis, C. A.; Oosterhoff, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 4589–4590.

(2) Schippers, P. H.; Dekkers, H. P. J. M. *Chem. Phys. Lett.* **1982**, *88*, 512–516.

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(4) This compound has been synthesized by Kokke[22] at these laboratories. Representative analytical data are as follows: ^{1}H NMR (CDCl$_3$, 100 MHz) δ 2.6–2.1 (6 H), 2.1–1.5 (8 H), 1.5–1.0 (2 H), complex spectrum; ^{13}C NMR (CDCl$_3$, 25 MHz) δ 216.96 (s), 44.99 (t), 43.77 (d), 35.13 (t); MS, *m/e* 192 (M$^+$); UV (nm, ε; CH$_3$CN) 315 (23), 305 (43), 295 (48), 288 sh (41); mp 213.5–215.5 °C.

(5) Prepared as follows: 1 g of *trans*-8-acetoxy[4.3.0]nonane-3,4-dione[22] was heated with 3.5 g of KOH and 7 g of H$_2$O in a Carius tube for 30 min at 125 °C. The reaction mixture was cooled to room temperature, diluted with water, and acidified to pH 1 with 1 N HCl. *trans*-3,7-Dihydroxybicyclo[3.3.0]octane-3-carboxylic acid was isolated by extraction with ethanol and subsequently refluxed with PbO$_2$/H$_2$SO$_4$. Extraction with CH$_2$Cl$_2$ yielded *trans*-7-hydroxybicyclo[3.3.0]octan-3-one (**2a**). Oxidation with pyridinium chlorochromate[23] yielded crude **2**. Purification of **2** proceded by extraction with ether and crystallization from ether. **2a**: ^{1}H NMR (CDCl$_3$, 100 MHz) δ 4.7 (quartet-like, 1 H), 2.7–2.2 (4 H), 2.2–1.2 (6 H), complex spectrum; ^{13}C NMR (CDCl$_3$, 25 MHz) δ 219.80 (s), 75.02 (d), 47.63 (d), 45.90 (d), 43.62 (t), 43.47 (t), 39.04 (t), 38.74 (t). **2**: ^{1}H NMR (CDCl$_3$, 100 MHz) δ 2.8–2.25 (4 H), 2.25–1.7 (6 H), complex spectrum; ^{13}C NMR (CDCl$_3$, 25 MHz) δ 215.99 (s), 45.08 (d), 43.26 (t); MS, *m/e* 138 (M$^+$); UV (nm, ε; CH$_3$CN) 318 (37.5), 308 (70), 297 (70), 289 sh (56); mp 165.5–166.5 °C.

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(11) Schippers, P. H., unpublished results.

(12) For a description of the instrument, see: Schippers, P. H.; Van den Beukel, A.; Dekkers, H. P. J. M. *J. Phys. E* **1982**, *15*, 945. The measurements were performed on ~1 × 10^{-2} M solutions in spectrograde CH$_3$CN. The bandwidth of excitation and emission was 20 nm.

(13) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; p 108.

(14) In the series of saturated cyclic ketones, cyclopropane and cyclobutanone excluded, fluorescence lifetimes[15] and fluorescence quantum yields ϕ_F[16] appear to be rather constant: $\tau_F \sim 2$–3 ns, $\phi_F \sim (1$–$2) \times 10^{-3}$. Moreover the values seem rather insensitive to alkyl substitution, except when it is at the α position.[15,16] With cyclopropanone[17] and cyclobutanone,[16,18] the values of τ_F and ϕ_F are an order of magnitude smaller than those observed for the higher homologues due to molecular predissociation processes. Since we found that the compounds **1**–**4** all have $\phi_F \sim 10^{-3}$, it seems reasonable to adopt the value $\tau_F \sim 2$ ns.

(15) Dalton, J. C.; Turro, N. J. *Ann. Rev. Phys. Chem.* **1970**, *21*, 499–560.

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polarization with **2** shows that here $k_{ET} \gtrsim 1 \times 10^{10}$ s^{-1}.

Rate of excitation energy transfer involves the interaction of the two locally excited states $\Psi_R\Psi_{S*}$ and $\Psi_{R*}\Psi_S$.[6,7,19] Since this interaction strongly decreases with carbonyl–carbonyl distance, it is not surprising that k_{ET} is much larger for the 1,5-dione than for the 1,7-dione. As far as we know the only data available on rate of intramolecular $^1n\pi^*$ energy transfer in aliphatic diketones are those of Lissi et al.[20] Interestingly, the rates they find for a series of nonrigid 1,4-diones ($\sim 2 \times 10^8$ s^{-1}) are much lower than that for the 1,5-dione **2**.

Although the reported measurements represent only a first step in the investigation of CPL as a probe for intramolecular energy transfer, the technique seems quite promising. Objects for further study are the extension of the dynamic range of the method by adding quenchers to affect τ_F and the influence of temperature and solvent. Further interesting possibilities include the study of intermolecular energy transfer in racemates from the dependency of $G_L - G_R$ on concentration and, as suggested at Groningen University,[21] the use of chemiexcitation to create the *meso*-dione's locally excited state in high enantiomeric excess.

Acknowledgment. We are grateful to J. P. M. van der Ploeg for the synthesis of **2** and to Dr. H. J. C. Jacobs for stimulating discussions.

Registry No. *meso*-**1**, 83998-83-8; *trans*-**2**, 83998-84-9; *trans*-**2a**, 83998-85-0; *trans*-**4**, 29365-79-5; *trans*-8-acetoxy[4.3.0]nonane-3,4-dione, 83998-86-1; bicyclo[3.3.0]octane-3,7-diol-3-carboxylic acid, 83998-87-2.

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(19) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836–850.

(20) Lissi, E. A.; Encinas, M. V.; Castañeda, F.; Olea, F. A. *J. Phys. Chem.* **1980**, *84*, 251–254.

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(22) Kokke, W. C. M. C., Ph.D. Thesis, Leiden, 1973.

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A Theoretical Prescription for Reductive Coupling of CO or CNR Ligands

Roald Hoffmann* and Charles N. Wilker

Department of Chemistry, Cornell University
Ithaca, New York 14853

Stephen J. Lippard*

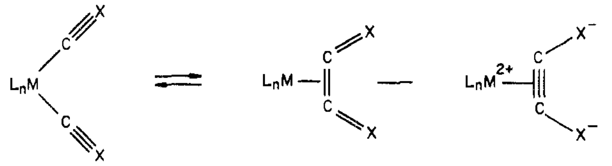
Department of Chemistry, Columbia University
New York, New York 10027

Joseph L. Templeton* and Douglas C. Brower

Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

Received September 27, 1982

Reactions that lead to carbon–carbon bond formation are always an attractive synthetic prospect. Especially valuable for such transition-metal catalyzed reactions are carbonyls or isocyanides, which are ubiquitous ligands. So let us think about the electronic requirements for coupling two CO or CNR ligands on a transition-metal center, reaction 1.[1]



1 X = O, NR

Many coordination numbers, geometries, metals, and electron counts could be envisaged and have been examined by us. We focus our discussion here on the seven-coordinate d^4 case, following an experimental observation—the only well-explored instance of C–C bond formation among thousands of carbonyl and isocyanide complexes occurs in the $[Mo(CNR)_6X]^+$ system.[2,3] Here the isocyanides couple in the presence of Zn and acid, with net addition of two H atoms to form $\{Mo[(CNHR)_2](CNR)_4X\}^+$, X = halide.

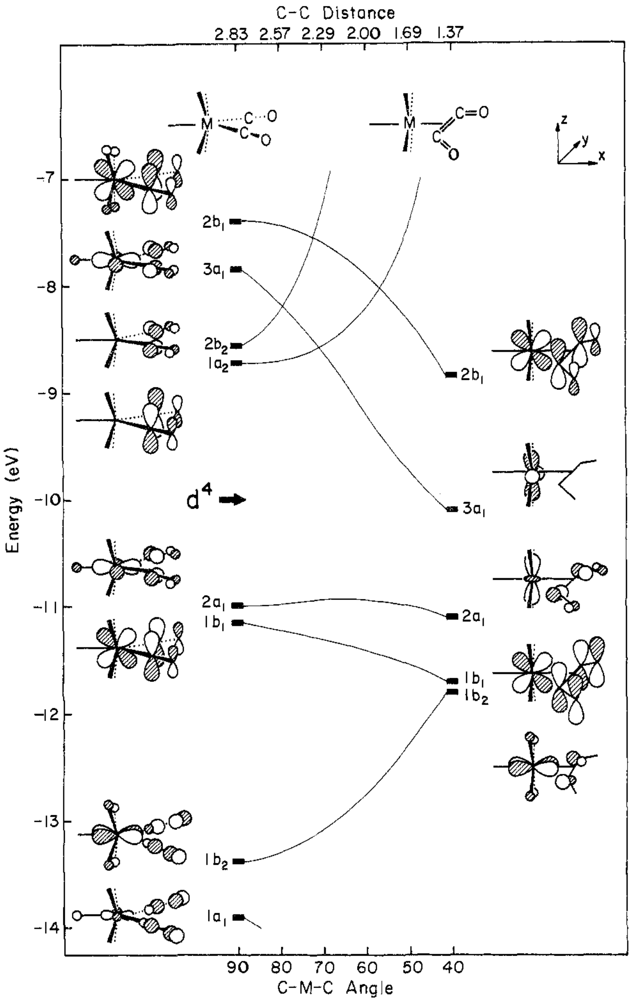


Figure 1. Evolution of energy levels in $H_5W(CO)_2^{3-}$ along an idealized coupling coordinate. The $2a_1$ level is the highest filled one for a d^4 electron count. Note the linear C–M–C angle scale at bottom and the corresponding nonlinear C–C distance scale at top.

Figure 1 shows the extended Hückel correlation diagram for the coupling of two carbonyls on W in a model $W(CO)_2H_5^{3-}$ ion, having a capped trigonal prismatic geometry.[4] The $1a_1$ and $1b_2$

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(1) The analysis is related to our previous study of carbene and carbyne coupling: Hoffmann, R.; Wilker, C. N.; Eisenstein, O. *J. Am. Chem. Soc.* **1982**, *104*, 632–634.

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(3) (a) For two examples of carbonyl coupling in binuclear complexes see: Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715. Bennett, M. J.; Graham, W. A. G.; Smith, R. A.; Stewart, R. P., Jr. *Ibid.* **1973**, *95*, 1684–1686. (b) Reductive coupling of coordinated CO in some highly reduced organometallics has been suggested: Ellis, J. E.; Parnell, C. P.; Hagen, G. P. *Ibid.* **1978**, *100*, 3605–3607. (c) For other examples of coupling coordinated ligands see the footnotes of ref 1. Two fascinating cases of carbyne–carbonyl coupling are to be found in the following work: Fischer, E. O.; Friedrich, P. *Angew. Chem.* **1979**, *91*, 345–346. Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766–768.

(4) These geometrical assumptions were made. When the reactant geometry is a capped trigonal prism, the C–M–C angle is 90°, the M–C–O angle is 180°, and the C–M–girdle ligand angle is 105°. When the product geometry is an octahedron with the newly formed C_2O_2 occupying one coordination site, the C–M–C angle is 40°, the M–C–O angle is 150°, and the C–M–girdle ligand angle is 90°. These three angles are varied linearly along the hypothetical reaction coordinate. All other angles and bond distances remain constant.

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