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CONTRASTING PHOTOCHEMICAL BEHAVIOR BETWEEN META-SUBSTITUTED AND PARA-SUBSTITUTED AROMATIC POLYCARBONYL COMPOUNDS[1]

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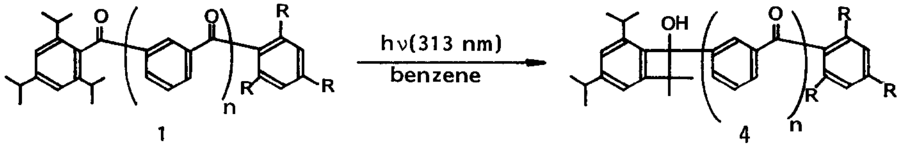
Summary: The meta-substituted polyketones 1b - f, including the parent ketone 1a, afforded approximately similar values for the quantum yield of benzocyclobutenol formation (Φ_{CB}), the triplet lifetime (τ), E_T, and λ_{max}, respectively. In contrast, Φ_{CB}, τ, E_T, and λ_{max} of the para-substituted polyketones 2a - c depended on their molecular structures.

Despite extensive photochemical study concerning monocarbonyl compounds,[2] that of conjugated polycarbonyl compounds is scarce.[3] We have studied the photocyclization of 2,4,6-triisopropylbenzophenone (1a) into the corresponding benzocyclobutenol 4a (eq 1) in great details.[4] By employing this reaction as a probe to monitor the excitation energy, we now investigated the photochemistry of aromatic polycarbonyl compounds 1 - 3. The results were quite different between the meta-substituted polyketones 1b - f and the para-substituted polyketones 2a - c.

As summarized in Table I, the compounds 1a - f exhibit absorption maxima at the virtually same regions, about 350 nm (n,π^*) and 235 nm (π,π^*), and the E_T values estimated from their weak (relative to benzophenone) phosphorescence spectra are nearly the same ($E_T \sim 69$ kcal/mol in ethanol at 77 K). The quantum yields for benzocyclobutenol formation (Φ_{CB}) and the triplet lifetimes (τ) obtained from linear Stern-Volmer quenching of the product 4 by 2,5-dimethyl-2,4-hexadiene (<0.05 M) are also approximately similar in this series ($\Phi_{CB} = 0.56 - 0.79$ and $\tau = 90 - 128$ ns, Table I). The high quantum yields for 1b - f indicate that the excitation decay from the nonreactive carbonyl chromophores (unstrained carbonyl groups) is not important.

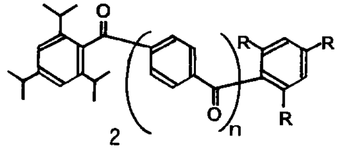
As compared with the meta-substituted polyketones, the para-substituted ones 2a - c exhibit a large red shift of the π,π^* absorption maximum (260 - 265 nm) with the similar n,π^* absorption maximum at ca. 350 nm. Furthermore, their E_T and Φ_{CB} are much lower than that of 1 and depend considerably on the number of the carbonyl group. The lowering of Φ_{CB} may be due to the probable increase of π,π^* character in their lowest triplet state. The observation that the triplet lifetime of 2b (51 ns) is about half that of 2a (91 ns) supports that the electronic excitation in the para-substituted compounds is delocalized over both of the carbonyl groups in the molecule.[5]

In the above situation , the rate of the triplet decay for the para-substituted polyketones will become the sum of the decay rates from the component carbonyl groups (eq 2). Thus the triplet lifetime may be reduced to approximately one-half by second triisopropyl substitution, as was observed for the pair 2a - 2b.



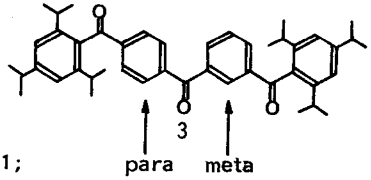
1 4 (1)

a, R = H, n = 0 ; b, R = H, n = 1; c, R = H, n = 2;
d, R = i-Pr, n = 1; e, R = i-Pr, n = 2; f, R = i-Pr, n = 3

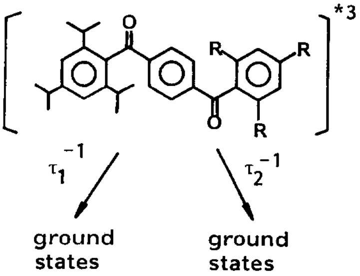


2

a, R = H, n = 1; b, R = i-Pr, n = 1;
c, R = i-Pr, n = 2

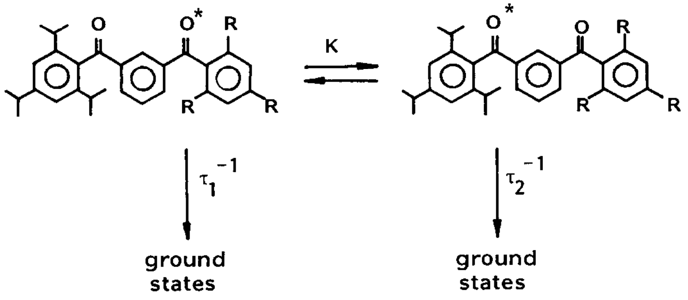


3



$$\tau^{-1} = \tau_1^{-1} + \tau_2^{-1} \qquad (2)$$

In contrast, the absorption and phosphorescence spectra of the meta-substituted compounds 1b - f indicate that each carbonyl group in a molecule is relatively independent because of the lack of conjugation. This fact and the observation that the τ values are almost irrelevant to the number of the triisopropyl substitution, as seen from comparison of each pair 1b (114 ns) - 1d (128 ns) or 1c (98 ns) - 1e (96 ns), suggest that their excited states may be better represented by a rapidly equilibrating mixture between localized excited states rather than by delocalization of the electronic excitation.[5] This situation is illustrated in the scheme below. The observed linear quenching plot with diene and the weak phosphorescence intensity support that the equilibrium is established.[6]



$$\tau = \frac{K + 1}{\tau_1^{-1} + K(\tau_2)^{-1}} \qquad (3)$$

Table I. Spectroscopic and Photochemical Properties of Aromatic Polycarbonyl Compounds.

compd	λ_{max}[a] nm (ε)	phosphorescence[b]		Φ_{CB}[c]	$k_q\tau$[c] M^{-1}	τ, ns	
		0-0 band kcal/mol	rel intensity			quen[c]	direct[d]
1a	242 (15700) 349 (63)	ca. 69 (68.5) 69.1#	0.022 (0.039)	0.60	450	90	332[e]
1b	233 (38000) 351 (152)	68.6 (67.6)	0.015	0.64	570	114	480
1c	234 (41500) 348 (290)	68.4 (67.6)	0.033	0.56	490	98	f
1d	232 (37500) 347 (185)	68.9 (67.9)	0.011 (0.043)	0.79	640	128	557
1e	233 (46000) 350 (260)	68.5 (67.9)	0.0077 (0.024)	0.76	480	96	f
1f	235 (63500) 350 (385)	68.5 (67.5)	0.0048	0.70	465	93	f
2a	260 (30000) 349 (170)	65.6	0.0064	0.16	455	91	380
2b	262 (32000) 350 (300)	f	f	0.10	255	51	f
2c	265 (68000) 346 (448)	64.5	f	0[g]	f	f	f
3	238 (16100) 260 (29100) 352 (337)	65.2	f	0.13	500	100	f
BP[i]	248 (19400) 346 (120)	68.9 (68.4) 68.6#	1.00 (1.00)	-	32500	6500	6900[h]
m-BBP[j]	247 (36800) 345 (230)	68.7 (67.8)	1.27 (0.70)	-	12500	2500	f
p-BBP[k]	260 (35000) 348 (359)	66.3 (65.4)	0.64	-	6000	1200	f

[a] In cyclohexane. [b] In ethanol at 77 K; maximum error, 0.2 kcal/mol. The values for methylcyclohexane glass are in parentheses. The values marked with # are in ether - pentane - ethanol (5 : 5 : 2) glass. [c] In degassed benzene at 25 °C; maximum error, 10 %. The reactions were stopped at a very low conversion in order to suppress the effect of back photoreaction and further photocyclization.[4c] For the consistency with our previous papers,[4] the quenching rate was assumed to be diffusion-controlled ($k_q = 5 \times 10^9\ M^{-1}s^{-1}$) and constant throughout the series in order to calculate τ(quen).[9] [d] Determined directly from laser photolysis in benzene by Drs. K. Hamanoue and T. Nakayama (Kyoto Institute of Technology). [e] 175, 191 and 225 ns in methanol, heptane and acetonitrile, respectively (Hayashi, H.; Nagakura, S.; Ito, Y.; Matsuura, T. Chem. Lett. 1980, 939). [f] Not determined. [g] No reaction. [h] Wolf, M. W.; Brown, R. E.; Singer, L. A. J. Am. Chem. Soc. 1977, 99, 526. [i] Benzophenone. [j] m-Benzoylbenzophenone. [k] p-Benzoylbenzophenone.

The steady-state treatment of the above scheme affords the relationship 3.[7] Thus the experimentally measured triplet lifetime τ should depend on the lifetimes of the localized excited states (τ_1 and τ_2) as well as on the equilibrium constant K. The only slightly longer τ value for 1b - f (93 - 128 ns) than that of the parent ketone 1a (90 ns) suggests a large K value (K > 1) for 1b - f. The high Φ_{CB} value for 1b - f may also arise from the large K value. This point will be explained in a subsequent paper.[8]

Finally we note that the compound 3 having meta- and para-substitution photocyclized only at the para-substitution site. The selective cyclization is interpretable in terms of usual "energy sink" concept, i.e., the para-substituted carbonyl group has a lower E_T value than the meta-substituted one, as readily seen from E_T of 2 and p-BBP (Table I).

References and Notes

(1) Photoinduced reaction, part 149.

(2) Turro, N. J. "Modern Molecular Photochemistry", Benjamin/Cummings: Menlo Park, Ca. 1978.

(3) (a) Wagner, P. J.; Siebert, E. J. J. Am. Chem. Soc. 1981, 103, 7329. (b) Herkstroeter, W. G.; Lamola, A. A.; Hammond, G. S. Ibid. 1964, 86, 4537.

(4) (a) Ito, Y.; Nishimura, H.; Umehara, Y.; Yamada, Y.; Tone, M.; Matsuura, T. J. Am. Chem. Soc. 1983, 105, 1590. (b) Ito, Y.; Matsuura, T. Ibid. 1983, 105, 5237. (c) Ito, Y.; Giri, B. P.; Nakasuji, M.; Hagiwara, T.; Matsuura, T. Ibid. 1983, 105, 1117.

(5) Results obtained from photoreduction of the diketones 1b, 2a, 3'-acetyl-1a and 4'-acetyl-1a with s-butylamine are consistent with this proposal (Ito, Y.; Kawatsuki, N.; Matsuura, T. Tetrahedron Lett. In press.).

(6) Energy migration between aromatic carbonyl groups is known to be rapid (intramolecular case, $>10^9\ M^{-1}s^{-1}$; intermolecular case, $>10^8\ M^{-1}s^{-1}$): (a) Wagner, P. J.; Nakahira, T. J. Am. Chem. Soc. 1973, 95, 8474. (b) Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. Ibid. 1980, 102, 727. (c) Maharaj, U.; Winnik, M. A. Chem. Phys. Lett. 1981, 82, 29. (d) Encinas, M. V.; Scaiano, J. C. Ibid. 1979, 63, 305.

(7) For kinetic analyses of bichromophoric systems, see Wagner, P. J.; Nakahira, T. J. Am. Chem. Soc. 1974, 96, 3668, and references therein.

(8) Ito, Y.; Kawatsuki, N.; Matsuura, T. Submitted for publication in this journal.

(9) Direct measurement by Dr. Hamanoue of τ for 1a, 1b, 1d and 2a (Table I) affords the k_q values 1.36×10^9, 1.19×10^9, 1.15×10^9 and $1.20 \times 10^9\ M^{-1}s^{-1}$, respectively, which are considerably slower than the diffusion rate. However, this result confirms the validity of the assumption that the same k_q value can be used throughout the compounds 1 - 3.

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