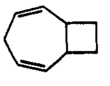
Table I. Thermolysis Rate Data for Some Selected Azo Compounds

Compd	Temp, °C	10^4k, $\sec^{-1}$	E_a, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate
1	+176.9	0.35			
	+189.0	1.14			
	+199.2	3.32	41.4 ± 0.3	+10.3	
	−3.5[a]	1.32×10^{-14}			8.8×10^2
2[b]	+240.0	212	44.6 ± 0.2	+10.5	
	−3.5				1
3[c]	+150.2	0.3	39.2 ± 0.3	+11	
	−3.5				6.7×10^4
4[c]	−3.5	1.71	14.9 ± 1.5	−21	1.1×10^{17}

[a] Extrapolated to −3.5° from the data at higher temperatures.[12] [b] Taken from ref 2 and 6. [c] Taken from ref 2.

summarized in Table I. Decomposition of **1** at 180° gave a product mixture consisting of 86% bicyclo[5.2.0]nona-2,5-diene (**8**)[13] and 14% of five other compounds.[14]



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The striking feature of the data in Table I is that decomposition of **4** is accelerated over that of **1** by $>10^{14}$. This represents one of the largest, if not the largest, rate factor yet observed between the two cyclopropyl configurations.[15–17] All available criteria clearly indicate that **1** decomposes by a diradical pathway without participation by the cyclopropane ring.[1–3,10,11c,18–21] It is evident from structural considerations that the changeover in mechanism which occurs in going from **4** to **1**[2,10] is a consequence of the differences in transition-state stereochemistry resulting from disrotatory opening of the edge cyclopropyl orbitals.[22] Models of the transition states based on "outward" rotation of participating cyclopropyl electrons clearly show perfectly aligned overlapping orbitals for the enormously accelerated **4** but orthogonally oriented orbitals with little or no overlap for **1**.[22] Participation with "inward" rotation of the cyclopropyl orbitals of **1** is improbable since it would lead to a severely strained transition state and a *trans,trans*-cycloheptadiene as product.[22] The results with **1** and **4** add an important calibration point to the evaluation of the influences of *endo*- and *exo*-cyclopropane orientations on chemical reactivity.

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(13) W. R. Roth, *Justus Liebigs Ann. Chem.*, 671, 10 (1964).

(14) The five products were present in approximately equal amounts. They have not been identified as yet because of the limited quantities available.

(15) The 10^2 reactivity difference between **1** and **3** suggests that the factor may be at least 10^{16}.

(16) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **89**, 1953 (1967); R. M. Coates and J. L. Kirkpatrick, *ibid.*, **92**, 4883 (1970).

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(21) J. A. Berson and S. S. Olin, *ibid.*, **91**, 777 (1969).

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Absolute Configuration of 1-Oxo[2.2]metacyclophane

Sir:

The stereochemistry of [2.2]metacyclophanes has attracted considerable attention.[1] We now wish to report the first absolute configurational assignment to a member of this family of compounds, 1-oxo[2.2]metacyclophane (**1**).[2]

The long-wavelength spectral region of (−)-**1** (Figure 1) is dominated by an intense negative Cotton effect centered near 318 nm, which corresponds to the lowest lying n → π* carbonyl transition (the R band) at 310–330 nm. The high rotational strength of this transition ($[\theta]_{\max}$ −36,700°) is in contrast to the relatively weak isotropic absorption, ε ~100 (after subtraction of the absorption tail).[3]

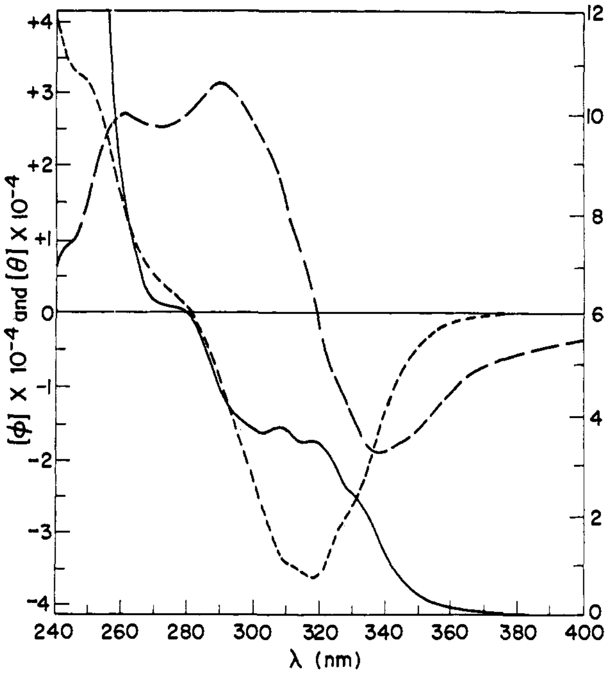


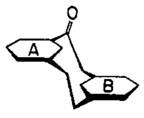
Figure 1. Spectral properties of (−)-1-oxo[2.2]metacyclophane (**1**) in isooctane solution: solid line, absorption spectrum (ordinate scale on the right); short dashes, circular dichroism; long dashes, optical rotatory dispersion (ordinate scale for the chiroptical properties on the left).

(1) For a recent review, see F. Vögtle and P. Neumann, *Angew. Chem., Int. Ed. Engl.*, 11, 73 (1972).

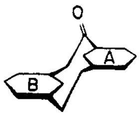
(2) H. W. Gschwend, *J. Amer. Chem. Soc.*, **94**, 8430 (1972).

(3) Also evinced in Figure 1 are two weakly positive Cotton effects at 280 and 250 nm. In addition, two strongly active transitions are centered at shorter wavelengths: a positive Cotton effect at 231 nm ($[\theta]_{\max}$ +63,100), and a negative Cotton effect at 207 nm (molecular amplitude (*a*) ~ −3600) corresponding to the strong absorption at 207 nm (ε 40,700).

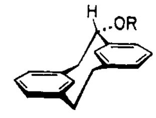
The benzoyl moiety in **1** is twisted about the phenyl-carbonyl (C_1–C_{15}) bond by *ca.* 60°. The sense of twist depends on the absolute configuration of **1**: in (*R*)-**1** the chirality of the twisted array is *P* and in (*S*)-**1** it is *M*.[4] It had previously been shown for a number of diterpenoid ketones and 6-oxoestrane derivatives[5] that the R band of twisted benzoyl chromophores is strongly active, and that the sign of the transition depends on the sense of twist: the *P* configuration corresponds to a positive and the *M* configuration to a negative Cotton effect. Accordingly, (−)-**1** has the *S* configuration.



(*R*)-**1**



(*S*)-**1**



2, R = H
3, R = *m*-BrC_6H_4CO

In the preceding analysis, the chromophoric properties of **1** were treated as essentially those of a conjugated ketone, with phenyl ring A supplying the α,β unsaturation.[5] Alternatively, **1** may be viewed as a homoconjugated ketone, with phenyl ring B supplying the β,γ unsaturation. The relative spatial disposition of the carbonyl group and phenyl ring B in **1** is remarkably similar in topography to that of the phenyl-carbonyl grouping in dimethyldibenzsuberone and related β,γ-unsaturated ketones, for which an extension of the octant rule was enunciated some years ago.[6] According to the extended rule the sign and intensity of the rotational strength of the R band of (−)-**1** are characteristic of a β,γ-unsaturated ketone chromophore corresponding in chirality to that of the composite carbonyl–phenyl B grouping in (*S*)-**1**.

The chiroptical properties of **1** *thus provide unambiguous evidence for the S configuration of* (−)-**1**, *regardless of whether the chromophoric entity is treated as an* α,β- *or* β,γ-*unsaturated ketone.*

This conclusion is supported by the results of an X-ray analysis of the *m*-bromobenzoate (−)-**3** derived from the equatorial alcohol (−)-**2**. As we have shown,[2] (−)-**1** is obtained by oxidation of (−)-**2** under retention of molecular chirality.

Crystals suitable for analysis were obtained by slow evaporation of an ether–hexane solution of **3**: mp 147°; $[\alpha]^{25}D$ −52.0° (*c* 1.17, $CHCl_3$); crystal data, orthorhombic, $P2_12_12_1$-$D_2{}^4$, a = 28.756 (13), b = 11.067 (6), and c = 5.821 (3) Å; d_{obsd} = 1.40 (5), $d_{X\text{-ray}}$ = 1.44 g cm^{-3} (Z = 4). A total of 1475 reflections were scanned using the θ–2θ technique and Cu Kα radiation on a Picker automated diffractometer taking care to preserve a right-handed coordinate system at all times; 1332 of these were judged to be above background. There was no significant decay in intensity of the six monitored reflections during the course of data collection. The structure solution was straightforward using heavy-atom Patterson and Fourier techniques. Both alternative configurations of the molecule were refined to convergence by full-matrix least squares including the anomalous dispersion contribution of the bromine atom and allowing anisotropic thermal motion for bromine and isotropic motion for the 25 carbon and oxygen atoms. The final values of the conventional and weighted *R* factors are summarized below.

Configuration	Conventional *R*	Weighted *R*
R	0.086	0.105
S	0.082	0.101

Application of the Hamilton statistical *R*-factor test[7a] to the weighted *R* factors gives a ratio of 0.105 : 0.101 or 1.04 for the hypothesis that configuration *R* is correct. This allows strong rejection[7b] of the hypothesis at even the 0.005 statistical significance level and clearly indicates that the *m*-bromobenzoate (−)-**3** and thus (−)-**2** possess the *S* configuration, in agreement with the conclusions of the chiroptical studies on the ketone (−)-**1**. Further refinement of the correct configuration allowing anisotropic thermal motion for all nonhydrogen atoms has resulted in a final *R* of 6.4%. Full details of this structure will be published elsewhere.[8]

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(4) Nomenclature according to R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966).

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(6) A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Amer. Chem. Soc.*, **84**, 1945 (1962).

(7) (a) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965). (b) There are 926 *hkl* reflections sensitive to the anomalous dispersion effects of the Br atom and 110 variables in the refinement. Therefore, $R_{1,816,0.005}$ = 1.005 from Table 1 in the above reference.

(8) A listing of structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-621.

Photochemically Induced Dynamic Electron Polarization of the Durosemiquinone–Phenoxy Radical Pair[1]

Sir:

Recently we have reported[2] the observation of chemically induced dynamic electron polarization of some photochemically produced 1,4-naphthosemiquinone radicals in liquid 2-propanol. We proposed a model in which the polarization is due to the optically spin-polarized triplets of the parent quinone. If the triplet depolarization rate *via* relaxation is comparable to the chemical hydrogen abstraction rate, then our model predicts that the resultant semiquinone radical and the counter radical will be in the emissive mode. A formal development of our model was given elsewhere.[3]

We originally proposed our model as an alternative

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(1) Chemically Induced Dynamic Electron Polarization Studies. III.

(2) S. K. Wong and J. K. S. Wan, *J. Amer. Chem. Soc.*, **94**, 7197 (1972).

(3) S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *J. Chem. Phys.*, in press.