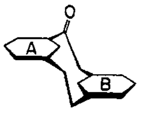
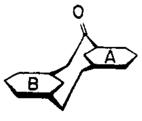
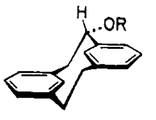
The benzoyl moiety in **1** is twisted about the phenyl–carbonyl (C_1–C_{15}) bond by *ca.* 60°. The sense of twist depends on the absolute configuration of **1**: in (*R*)-**1** the chirality of the twisted array is *P* and in (*S*)-**1** it is *M*.[4] It had previously been shown for a number of diterpenoid 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).

(5) R. C. Cambie, L. N. Mander, A. K. Bose, and M. S. Manhas, *Tetrahedron*, **20**, 409 (1964); G. Snatzke, *ibid.*, **21**, 439 (1965).

(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.

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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.

to the established "radical-pair" theory. Subsequently, we realized[2] that our model and the radical-pair theory would differ in one important respect. The radical-pair theory predicts that the semiquinone radical and the counter radical, which arises from the H atom abstraction, would have *opposite* electron polarization.[4] Our model predicts the *same* spin polarization. To the best of our knowledge, there has been no reported experimental observation on the CIDEP behavior of both radicals. In this communication we report such experimental observations; the results indicate that the semiquinone and the counter radical have the *same* polarization.

In the photochemical system of 1,4-naphthoquinone in 2-propanol, the short-lived $(CH_3)_2COH$ counter radical has eluded experimental detection. One of the reasons that the 2-propanol radical is difficult to detect is that it readily reacts with quinones to form semiquinones.[5] Thus, it may be possible to observe a more "stable" counter radical if there were a hydrogen donor which would react *rapidly* with the spin-polarized triplet quinone.

In order to arrive at definite conclusions about the spin polarization of both the semiquinone radical and the counter radical, it is necessary to monitor both radicals simultaneously. Consequently, the esr spectra of the radical pair must have some nonoverlap components so that their decay can be measured separately at different magnetic fields.

With the previous considerations in mind, we chose to carry out our investigation in a photochemical system of duroquinone in acetic acid in the presence of a highly reactive hydrogen donor, namely, the 2,6-di-*tert*-butylphenol. For this system we observed CIDEP in both the durosemiquinone radical and the 2,6-di-*tert*-butylphenoxy radical. We established that all hyperfine components of *both* radicals exhibit the same emissive behavior. A typical decay curve for the phenoxy counter radical is shown in Figure 1. This observation confirms a prediction of our earlier theoretical model.[3] We also carried out control experiments to confirm that the phenoxy radicals were not generated by direct photolysis of the phenol in our present system using all Pyrex optics and cells.

In addition to finding both the semiquinone radical and the counter phenoxy radical in the emissive mode, we also observed the following. The initial emission of the phenoxy radicals was enhanced by increasing concentration; this is due to the increase of hydrogen abstraction rate when the spin depolarization rate is relatively constant in the given system. In acetic acid, the photochemical reaction gives a steady-state concentration of phenoxy radicals which is greater than that of the semiquinone radicals. However, the reverse is obtained when *tert*-butyl alcohol is used as solvent.

We have observed that the CIDEP behavior of the semiquinone radical and the phenoxy counter radical is to some degree dependent on solvents. At present we cannot explain the effect of solvents on actual photochemical reactions. Nonetheless, the present results do suggest that our previously discussed model[2,3] is at least qualitatively correct. Further detailed and systematic studies will follow.

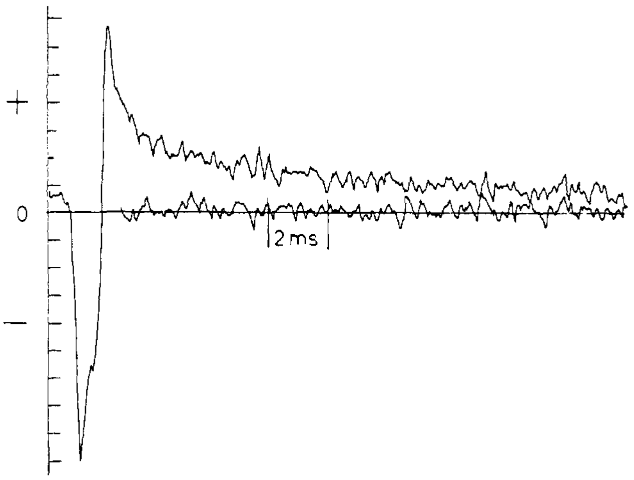

Figure 1. Time dependence of the esr signal intensity at constant magnetic field of the 2,6-di-*tert*-butylphenoxy radicals produced from the photolysis of duroquinone and the parent phenol in acetic acid: absorption mode (+), emission mode (−).

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[4] F. J. Adrian, *J. Chem. Phys.*, **54,** 3918 (1971).

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An Approach to Tetrahedrane. Pyrolysis of the Dilithium Salt of *trans*-Butenedial Bistosylhydrazone

Sir:

As a possible precursor of tricyclo[1.1.0.0^{2,4}]butane (IV, tetrahedrane), the title compound (Ia) has been prepared. Pyrolysis of Ia, by immersion of the pyrolysis vessel, under evacuation through a series of traps cooled at −80° and with liquid nitrogen, into a bath held at 140°, was complete within 1–1.5 min. This procedure is a modified version of that of Kaufman, *et al.*[1]

The condensate at −80° was entirely THF, in which Ia was prepared. The absence of butenyne, benzene, cyclooctatetraene, and *syn*-$\Delta^{3,7}$-tricyclo[4.2.0.0^{2,5}]octadiene was verified by glpc. It is therefore clear that cyclobutadiene is not formed.[2] The material condensable with liquid nitrogen, but not at −80°, contained acetylene[3] and 1–1.5% ethylene. In later experiments with Ib, the ethylene was collected by preparative glpc and found to contain no deuterium. Thus, acetylene is the *only* volatile product of pyrolysis of Ia. The residue was not examined in detail; however, it was apparent that some polymerization had occurred.

To investigate the intermediate(s) responsible for acetylene, deuterium labeling experiments were performed. 2,5-Furan-d_2, from deuterolysis[4] of 2,5-

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[1] G. M. Kaufman, J. A. Smith, G. G. Vander Stouw, and H. Schechter, *J. Amer. Chem. Soc.*, **87,** 935 (1965).

[2] E. Hedaya, R. D. Miller, D. W. McNeil, P. F. D'Angelo, and P. Schissel, *ibid.*, **91,** 1875 (1969).

[3] A 20–30% variable yield which seemed to be dependent on the fineness of subdivision of powdered Ia.

[4] B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discuss. Faraday Soc.*, **19,** 30 (1955).