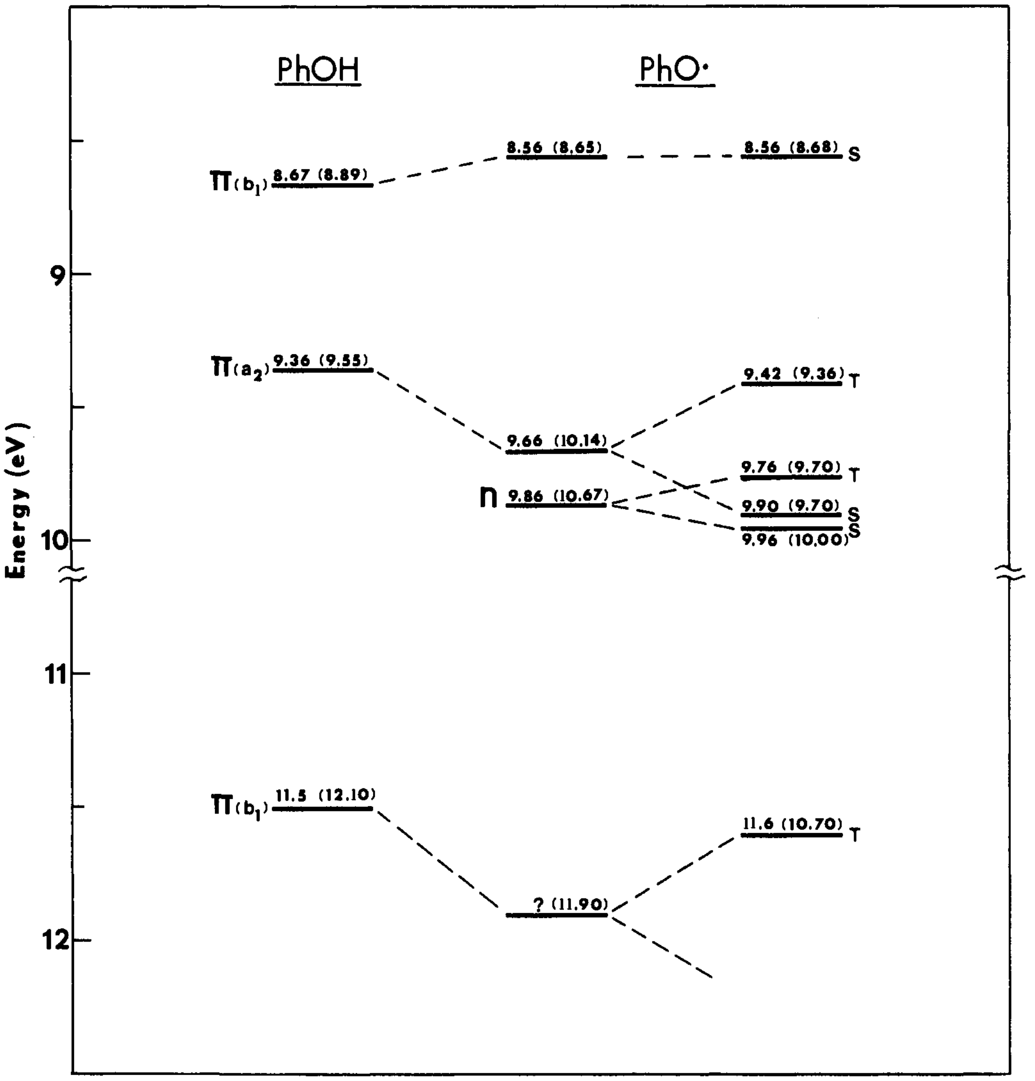

Figure 2. Correlation diagram relating the observed ionization energies (MNDO values in parentheses) for PhOH with those of PhO· (**1**). The central column compares means of corresponding S–T pairs with (in parentheses) MNDO values while the last column compares the observed ionization energies with (in parentheses) those calculated by UMNDO and reduced by 1 eV to allow for the systematic error noted in the text. For a discussion of the high-lying oxygen lone-pair orbital in **1** see ref 11.

first T and S ionizations of **9**.[14]

The heat of formation of phenoxy cation [$\Delta H_f(\mathrm{PhO^+})$] can be calculated from the adiabatic ionization energy and heat of formation of phenoxy radical. Using our value (8.56 ± 0.02 eV; 197.4 ± 0.5 kcal/mol) for the former and the most recent value (11.6 ± 2.3 kcal/mol[18]) for the latter, we find

$$\Delta H_f(\mathrm{PHO^+}) = 209.0 \pm 2.8 \text{ kcal/mol} \qquad (2)$$

This compares with values calculated by MNDO (203.2 kcal/mol) and estimated by mass spectrometry (≤224 kcal/mol[5]).

Our conclusions are currently being tested by further studies of the thermolysis of **2** and its derivatives and of the analogous phenyl benzyl ethers.

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(14) The first ionization energy of **9** has been estimated by mass spectrometry to be 8.56,[15a] 8.69 ± 0.1,[15b] or 8.41 eV.[15c] The S–T separation of the resulting ion is estimated by MINDO/3 to be 1.6 kcal/mol for the ground states[16] and 14.7 kcal/mol for ions with D_{5h} symmetry.[17] The difference between the two vertical ionizations of **9** is estimated by UMNDO to be 0.22 eV.

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Asymmetric Synthesis in a Spinning Vessel

Sir:

A recent communication[1] claims the achievement of asymmetric synthesis in a spinning vessel. This result is very surprising because it violates the gravitational analogue of de Gennes' theorem[2,3] on

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the impossibility of asymmetric synthesis in a static electromagnetic field. The essence of de Gennes' theorem is that a Hamiltonian involving external static fields $\vec{E}$ and $\vec{B}$ is invariant under the combined symmetry of a time reversal, T, and a reflection, R, through a plane containing $\vec{E}$ and $\vec{B}$. Indeed, $\vec{E}$ is invariant, and $\vec{B}$ changes sign under each one of these operations.[4] Likewise, the gravitational field $\vec{g}$ is invariant, and the spinning velocity $\vec{\omega}$ changes sign under T or R. (This analogy is not a coincidence: a magnetic field $\vec{B}$ is actually due to the rotational motion of electric charges.) Thus, the Hamiltonian of a molecule in a spinning vessel is invariant under TR, and all the energy eigenstates and equilibrium distributions must also be invariant under TR.

In plain language, if we make a movie of the rotating vessel and then run that movie backward in time *and* reflected in a vertical mirror, we see the *same* $\vec{g}$ and $\vec{\omega}$. Since the reversed-reflected movie is identical with the original one, there can be no preponderance of left handed or right handed molecules, as the latter are interchanged by R and invariant under T.

However, a vessel *rotating in a static electromagnetic field* (for example, with $\vec{E}$, $\vec{B}$, and $\vec{\omega}$ perpendicular to each other) could in principle lead to asymmetric synthesis, because the pseudoscalar $\vec{\omega}\cdot(\vec{E} \times \vec{B})$ changes sign under any space reflection, but not under T. (From the point of view of a rotating observer, this would be seen as a rotating electromagnetic field, like in a beam of circularly polarized light.) The same is also true for $\vec{\omega}$, $\vec{g}$, and the natural magnetic field of the Earth, but the latter seems too weak to have an appreciable effect. In natural units ($\hbar = e = m_e = 1$), we have $g \sim 10^{-22}$, $B(\text{Earth}) \sim 10^{-8}$, $\omega(\text{Earth}) \sim 10^{-21}$, and $\omega(\text{ref } 1) \sim 10^{-14}$.

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Quintet State Triplet–Triplet Radical Pairs. 2

Sir:

We recently reported the first detection of a quintet state radical pair.[1] Prior to that, radical pairs had only been seen in the triplet state.[2,3] The quintet radical pair was observed in the low-temperature photolysis of azibenzil where the apparent primary products are the cis and trans conformers of triplet benzoylphenylmethylene, **1a** and **1b**.[4] Two near-neighbor triplets can interact to form a quintet radical pair, **Q1**. Upon warming, the quintet is irreversibly converted to a new triplet, with small D and E values, which was identified as a diradical formed via spin conversion and pairing of two unpaired electrons.

We now wish to report an additional quintet state radical pair obtained in the low-temperature, $T \leq 77$ K, $\lambda \geq 345$ nm, photolysis of 9-diazo-10-anthrone (**2a**) powder.

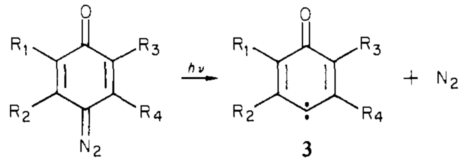
Table I. Zero-Field Splitting Parameters[a]

species	D, cm^{-1}	E, cm^{-1}	ref
1a	0.3916	0.0518	4
Q1	0.0943	0.0077	1
3a	0.3638	0.0176	this work
Q2	0.118 ± 0.005[b]	0.0065 ± 0.0022[b]	this work
3b	0.3179	0.0055	5
3c	0.3284	0.0086	5
3d	0.3470	0.0010	5
3e	0.3333	0.0112	5

[a] $g = 2.002$ was used as the best fit of **3a** and **Q2**. [b] The spectrum was reproduced within these errors.

A complex ESR spectrum (Figure 1) having a distribution pattern similar to that of the azibenzil case[1,4] was observed on irradiation and could be resolved into three different spectra: (1) an intense signal with no hyperfine structure at $g = 2.003$, which is clearly a secondary photolysis product (Figure 2) and is assigned to an unidentified doublet radical; (2) a set of four absorptions (~590, 4495, 5179, and 7166 G at $\nu = 9.167$ GHz) which is assigned to the randomly oriented triplet state of the carbene radical formed as an apparent primary product; (3) a set of absorptions consisting of at least 10 lines of weak intensity, appearing in the 100~5600-G range.

The triplet spectrum gives zero-field splitting parameters similar to those of the triplets **3b–e**



2 **3**

a, $R_1 + R_2 = R_3 + R_4 = -C_4H_4-$
b, $R_1 = R_2 = R_3 = R_4 = H$
c, $R_1 = R_3 = Cl$, $R_2 = R_4 = H$
d, $R_1 = R_3 = H$, $R_2 = R_4 = Cl$
e, $R_1 + R_2 = -C_4H_4-$, $R_3 = R_4 = H$

from the photolysis of benzene 1,4-diazo oxides, **2b–e** as reported by Wasserman and Murray[5] (Table I).

Finally the third, complex spectrum is assigned to a randomly oriented quintet state radical pair, **Q2**, formed through the interaction of two near-neighbor triplet carbenes. The zero-field splitting parameters of the quintet can be obtained from the Hamiltonian

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D\{S_z^2 - (S(S + 1))/3\} + E(S_x^2 - S_y^2)$$

where $S = 2$.

When first-order perturbation theory is used, the high-field limit and the next highest absorption of the quintet state are expressed as $H_z = H_0 + 3D/g\beta$ and $H_y = H_0 + 3(D + 3E)/2g\beta$, respectively, with $D > 3E$ and $H_0 \sim 3300$ G. Assuming that H_z is missing probably because of its weak signal intensity and close location to the strong highest field absorption of **3a** and that the highest steplike absorption of the quintet observed corresponds to H_y, the exact energy levels of $\mathcal{H}$ obtained by a numerical iteration method were used to determine the zero-field splitting parameters (Table I) from the above two absorption fields. The D and E values obtained (Table I) then reproduce the observed spectrum reasonably well. When it is assumed that the highest observed line corresponds to H_z, the distribution of the experimental spectrum could not be satisfactorily reproduced. The strongest absorptions, which correspond to $|m| = 0 \rightleftarrows |m| = 1$ transition of the quintet, occur around 2500 G. These absorptions are superimposed on the double quantum transition of **3a** at the magnetic field predicted[6] by the values of D and E. However, by attenuating the

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