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(Earth) $\sim 10^{-8}$, ω(Earth) $\sim 10^{-21}$, and ω(ref 1) $\sim 10^{-14}$.

Acknowledgment. I am grateful to E. A. Halevi for calling my attention to this problem.

---

(3) Mead, C. A.; Moscowitz, A. *Tetrahedron Lett.* **1977**, 1063.

(4) Sakurai, J. J. "Invariance Principles and Elementary Particles", Princeton University Press: Princeton, 1964.

Asher Peres
Department of Physics
Technion—Israel Institute of Technology
Haifa, Israel

Received May 20, 1980

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.

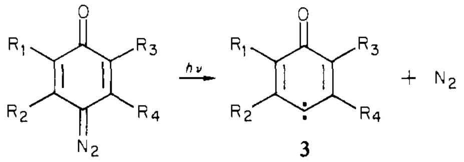
Table I. Zero-Field Splitting Parameters[a]

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

---

(1) Murai, H.; Torres, M.; Strausz, O. P. *J. Am. Chem. Soc.* **1980**, *102*, 5104.

(2) Kurita, Y. *J. Chem. Phys.* **1964**, *41*, 3926; Wiersma, D. A.; Kommandeur, J. *Mol. Phys.* **1967**, *13*, 241; Ohigashi, H.; Kurita, Y. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 704; Symons, M. C. R. *Nature (London)* **1967**, *231*, 1226. Geoffroy, M.; Lucken, E. A. C. *Helv. Chim. Acta* **1970**, *53*, 813.

(3) Gordy, W.; Morehouse, R. *Phys. Rev.* **1966**, *151*, 207. Niizuma, S.; Kokubun, H.; Koizumi, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 335. Arimitsu, S.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1357.

(4) Murai, H.; Torres, M.; Strausz, O. P., to be submitted for publication.

(5) Wasserman, E.; Murray, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 4203.

(6) de Groot, M. S.; van der Waals, J. H. *Physica (Amsterdam)* **1963**, *29*, 1128; Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

0002-7863/80/1502-7390$01.00/0

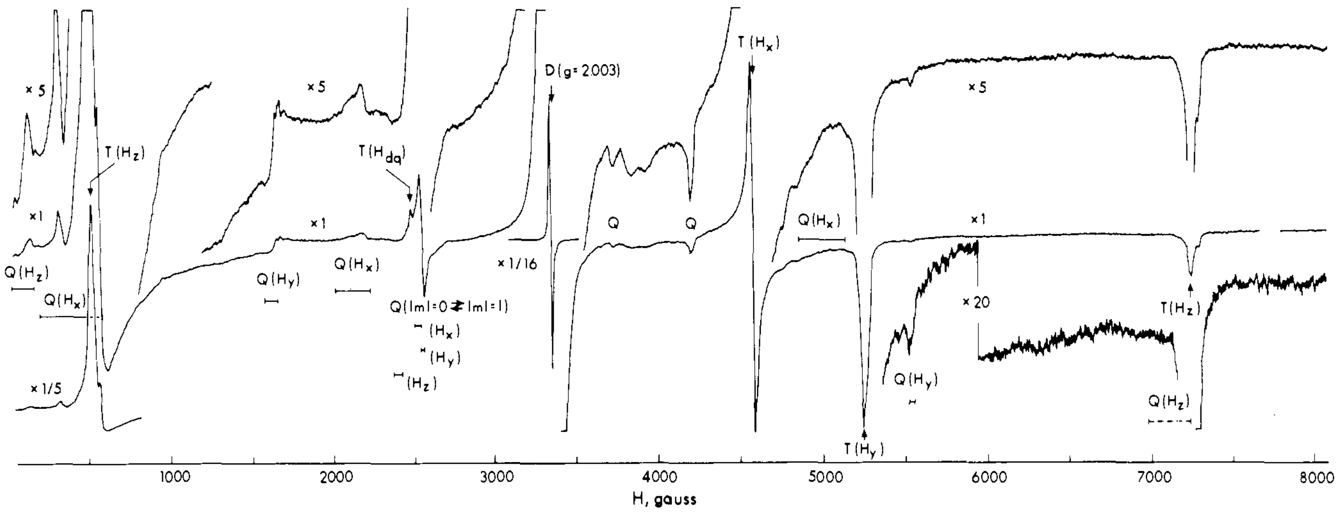


Figure 1. EPR spectrum of triplet carbene, T (H_z, H_x, H_y, H_z, H_{dg}), quintet radical pair, Q ($H_{x,y,z}$), etc., and unidentified doublet radical D generated in the $\lambda \geq 345$ nm photolysis of 9-diazo-10-anthrone powder at 77 K and recorded at 20 K. The klystron frequency was 9.368$_5$ GHz. The error bars indicate the range of reproduced resonance lines which have been positively assigned.

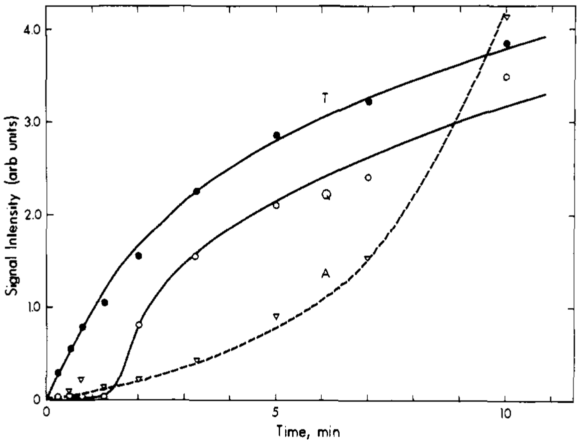


Figure 2. Time dependence of the ESR signals during photolysis of 9-diazo-10-anthrone powder at 77 K. T = **3a**; Q = **Q2**; A = doublet radical.

microwave power intensity it is possible to clearly distinguish between these two different spectra, as seen from Figure 3.

Exposure time studies (Figure 2) showed that the ESR absorption of **3a** was linear with time, while the intensity of the quintet spectrum featured some induction period in the initial stage. This result is similar to that of the azibenzil case and is consistent with the postulate that the quintet species is formed from the interaction of two triplets of **3a**.

All these ESR signals are stable for hours at 77 K, but when the photolysate is warmed to 160 K, both **3a** and the quintet signals fade slowly. The quintet decays somewhat faster than **3a**. Conversion of the quintet spectrum to a new triplet spectrum which was observed in the case of azibenzil[1] did not occur here. A weak signal corresponding to a $\Delta m = 2$ transition of a triplet having small zero field parameters ($D^* = (D^2 + E^2)^{1/2} \sim 0.020$ cm^{-1}, from $H_{\min}$) was observed, while the $\Delta m = 1$ transition was obscured by the superimposed strong absorption of the doublet radical. However, this $H_{\min}$ seems to coexist with one of the quintet signals before annealing. The origin of this triplet has not been established.

The apparent signal growth which was observed in the azibenzil case[1] in the dark immediately after cessation of irradiation was not observed in the present case. Photolysis of **2a** in an ethanol glass matrix produced only **3a** and the doublet radical.

In summary, it may be stated that the quintet state radical pair formed between two triplet carbenes from the photolysis of 9-diazo-10-anthrone reported here provides an additional example of a quintet state radical pair to the one reported earlier, from the interaction of two triplet benzoylphenylmethylenes.

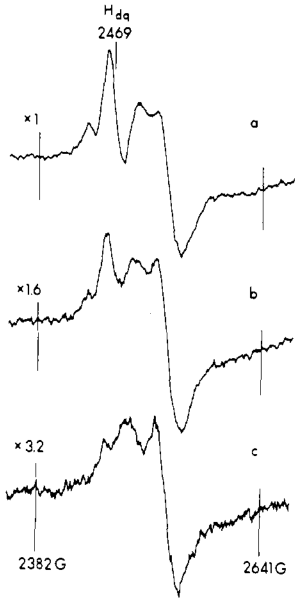


Figure 3. Microwave power dependence of the ESR spectra of the quintet and the doublet quantum transition of **3a** (H_{dq}) at 14 K. Attenuation: (a) 7, (b) 12, and (c) 20 dB at a klystron frequency of 9.371 GHz.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for continuing financial support.

H. Murai, M. Torres, O. P. Strausz*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada T6G 2G2

Received May 16, 1980

An Efficient, High Conversion Photoinduced Emulsion Polymerization. Magnetic Field Effects on Polymerization Efficiency and Polymer Molecular Weight

Sir:

An emulsion polymerization (EP) typically involves four fundamental ingredients: (1) an aqueous dispersion medium, (2) dispersed droplets of monomer, (3) a micelle-generating detergent,

0002-7863/80/1502-7391$01.00/0