1,3-DIPHENYL-1,3-CYCLOPENTANEDIYL:
A REMARKABLY STABLE LOCALIZED BIRADICAL

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Abstract: The triplet ground state of 1,3-diphenyl-1,3-cyclopentanediyl (3) has
been directly observed by matrix-isolation EPR spectroscopy at both 4 K and 77 K.

Until recently, the direct observation of localized, hydrocarbon biradicals was quite uncommon. Cyclopentanediyl (1) and some simple methyl derivatives were first observed in their triplet states by Closs in 1975,[2] and for some time these remained the only examples.[3] The cyclopentanediyls observed were quite unstable, decaying via quantum-mechanical tunneling even at 5 K. In addition, several simple methyl-substituted structures could not be observed at all, suggesting that this system was very much on the edge with regards to lifetime under cryogenic, matrix-isolation conditions. In contrast, we recently reported the observation of a broad series of cyclobutanediyls (2).[4] Cyclobutanediyls with only simple alkyl substituents (R = methyl, ethyl, propyl) also decayed via tunneling at all temperatures.[5] However, those with delocalizing substituents (vinyl or phenyl) are stable from 4 to roughly 20 K. Above 20 K, conventional Arrhenius decay commences, with some structures being marginally observable at temperatures as high as 60 K.[5] Based on these observations we concluded that the four-ring system was inherently more stable than the five.[4b] We now report the surprising observation that 1,3-diphenyl-1,3-cyclopentanediyl (3) is much more stable[6] than any of these previously reported systems. Intense signals of the triplet can be generated readily even *at 77 K!*
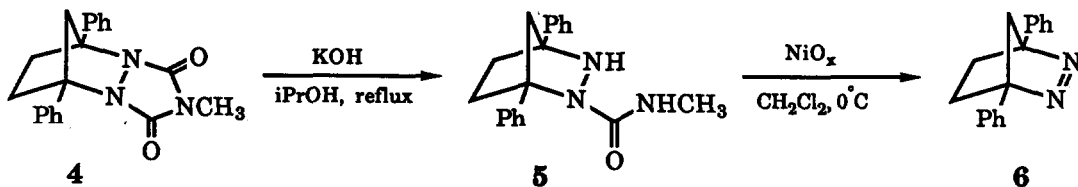

1   **2**   **3**

The precursor to 3, diazene 6, is easily prepared. Urazole 4[8] is obtained by hydrogenation of the Diels-Alder adduct of N-methyltriazolinedione and diphenylcyclopentadiene.[9] As in other cases,[4,10] we have found that the two-step procedure involving partial hydrolysis to the semicarbazide (5)

4   **5**   **6**

followed by oxidation with nickel peroxide is the method of choice for the preparation of thermally sensitive azoalkanes. Diazene 6 has been fully characterized,[8] and is adequately stable, with a half-life of 45 min at 35 °C.

Photolysis (323–345 nm) of a frozen 2-methyltetrahydrofuran (MTHF) solution of 6 at 3.8 or 77 K in the cavity of an EPR spectrometer produces the characteristic triplet spectrum of Figure 1. The zero-field splitting (zfs) values, along with those for relevant reference compounds, are shown in Table I. The zfs values for 3 are completely in line with expectation. Our previously described semi-empirical approach[11] with scaling to the values for 2[4b] had predicted $|D/hc| = 0.048$ cm^{-1} long before the spectrum was observed. Remarkably, the ratios of D values 1 to 2-Me and 3 to 2-Ph are identical, with a value of 0.75. This indicates that the delocalizing effects of phenyl are identical in the two systems. These observations strongly indicate that any geometry changes that occur upon substitution must be the same in both systems. The most plausible conclusion is that substitution does not produce any geometry change, and that all the triplet biradicals of Table 1 are planar, or effectively planar.[12] We assume that 3 has a triplet ground state, based on the fact that it is readily observable at 3.8 K.

As with most cyclobutanediyls 2 and with 1, the $\Delta m_s = 2$ region of the spectrum for 3 clearly shows splitting due to hyperfine coupling (hfc). Figure 2 shows this splitting and the simulation obtained using our previously described procedure.[4b] In our studies of 2 we demonstrated that the ring CH$_2$ groups exhibited hyperfine splittings that are equivalent in magnitude to those seen for analogous free radicals.[4b,13] This is in contrast to the hfc seen in most triplets, which produces splittings that are half those seen in radicals.[14] This result is a consequence of the fact that the ring CH$_2$ groups in 2 are in the unique position of being able to, in effect, couple simultaneously to both radical centers. The splitting in 3 provides a further opportunity to test this reasoning, and the hfc constants of Figure 2 fully support the analysis. The hydrogens at C2 show a full splitting similar to that seen in 2-Ph. Those at C4 and C5 produce couplings that are essentially one half those for C2.

Triplet biradical 3 is indefinitely stable at 4 K. In contrast to 1 and all derivatives of 2, quite strong signals of 3 can easily be generated at 77 K, but the EPR signal does decay *very* slowly at this higher temperature. A full kinetic analysis is in progress, but we estimate a half-life on the order of hours at 77 K. This makes 3 by far the most persistent localized, hydrocarbon biradical yet observed, and suggests that localized systems that persist up to even higher temperatures could be designed.

Obviously our previous arguments[4b] concerning the apparent greater stability of the cyclobutanediyls *vs.* the cyclopentanediyls, which emphasized the greater singlet-triplet gap and reduced conformational flexibility of the former, must be discarded. We now have the first direct comparison of identically substituted systems — 3 *vs* 2-Ph — and the cyclopentanediyl is clearly more stable, kinetically. It has long been recognized that the thermodynamic driving force for ring closure is much less in the cyclopentanediyl than in the cyclobutanediyl, but at this stage it is perhaps best to wait until more quantitative data are available before invoking this factor. Further studies of 3 and of the ambient temperature thermal chemistry and photochemistry of 6 are in progress.
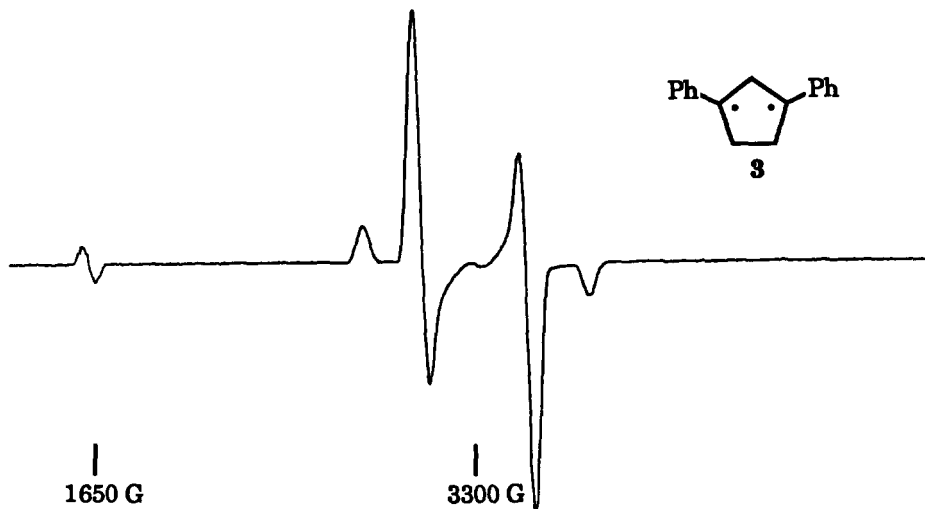
Figure 1. EPR spectrum of **3** generated by direct photolysis (λ 323-345 nm) of **6** in an MTHF matrix at 77 K.

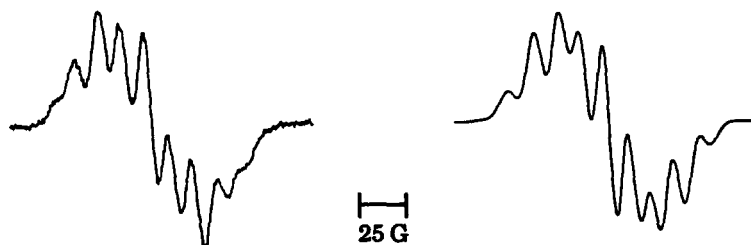**Figure 2.** Observed (left) and calculated (right) hyperfine patterns of the $\Delta m_s = 2$ transition of biradical **3**. The coupling constants used in the simulation are 24G (2 H, methano), 14G (4 H, ethano), 3G (6 H, ortho, para). The limitations and complications of simulating hyperfine patterns of triplet powder spectra are discussed in detail elsewhere.[4b]

Table I. Zero-Field Splitting Parameters (cm⁻¹) for Localized Biradicals

	1	**3**	**2-Me**	**2-Ph**
|D/hc|	0.084	0.045	0.112	0.060
|E/hc|	0.002	0.001	0.005	0 002

References

(1) JPL–CSMT Fellow, 1987-1988.

(2) Buchwalter, S.L.; Closs, G.L. *J Am Chem Soc* **1975**, *97*, 3857-3858. Buchwalter, S.L.; Closs, G.L. *J. Am Chem Soc.* **1979**, *101*, 4688-4694.

(3) Although not purely hydrocarbons, a series of triplet 4,5-diaza-1,3-cyclopentanediyls were the first localized organic biradicals to be characterized by EPR. (Arnold, D.R.; Evnin, A.B.; Kasai, P.H. *J Am. Chem Soc* **1969**, *91*, 784-785) The radical centers are in conjugation with a urazole ring, and comparison of the zfs values reported with those described here indicate a considerable, but variable degree of delocalization into the urazole.

(4) (a) Jain, R.; Snyder, G.J.; Dougherty, D.A. *J. Am Chem Soc* **1984**, *106*, 7294-7295. (b) Jain, R.; Sponsler, M.B.; Coms, F.D.; Dougherty, D.A. *J Am Chem. Soc* **1988**, *110*, 1356-1366.

(5) Sponsler, M.B.; Jain, R.; Coms, F.D.; Dougherty, D.A., manuscript in preparation.

(6) Strictly speaking, we are addressing the extent to which the biradicals 1-3 are *persistent*[7] under matrix-isolation conditions It is assumed that the diphenyl compounds are *stabilized*[7] relative to their fully localized counterparts We use *stable* in the phenomenological sense, meaning observable and long-lived (hours) at a given temperature

(7) Griller, D.; Ingold, K.U. *Acc Chem Res* **1976**, *9*, 13-19.

(8) 4: ^{1}H NMR (CDCl$_3$) δ 2.35 (d, 1 H, $J=10.5$ Hz), 2 39 (m, 2 H), 2.65 (m, 2 H), 2 93 (dt, 1 H, $J=10$ 5, 2.7 Hz), 3 01 (s, 3 H), 7.40 (m, 6 H), 7.60 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 25.38 (q, $^1J_{CH}=141.6$ Hz), 31.54 (t, $^1J_{CH}=133.9$ Hz), 56.38 (tt, $^1J_{CH}=140.1$ Hz, $^3J_{CH}=5.9$ Hz), 73.78 (s), 126.79 (d, $^1J_{CH}=160.7$ Hz), 128.45 (d, $^1J_{CH}=159.9$), 128.50 (d, $^1J_{CH}=159.9$), 135.06 (s), 156.15 (s); exact mass calcd: 333.1477, found· 333.1480. 6· ^{1}H NMR (CDCl$_3$, -15 °C) δ 1 59 (m, 2 H), 1.80 (dt, 1 H, $J=10.5$, 2.4 Hz), 2.06 (d, 1 H, $J=10.5$ Hz), 2.09 (m, 2 H), 7.45 (m, 6 H), 7.68 (m, 4 H); ^{13}C NMR (CDCl$_3$, -15 °C) δ 30.21 (t, $^1J_{CH}=137.9$ Hz), 48.51 (tt, $^1J_{CH}=136.1$ Hz, $^3J_{CH}=5.5$ Hz), 91.32 (s), 126.77 (d, $^1J_{CH}=160.7$ Hz), 127 97 (d, $^1J_{CH}=161$ 4 Hz), 128.67 (d, $^1J_{CH}=159.5$ Hz), 137.95 (s); UV (MTHF) $\lambda_{max}=350$ nm.

(9) Drake, N.L.; Adams, J.R , Jr. *J Am Chem. Soc.* **1939**, *61*, 1326-1329.

(10) Snyder, G J ; Dougherty, D.A. *J Am Chem Soc.* **1985**, *107*, 1774-1775. Kaisaki, D.A.; Dougherty, D.A. *Tetrahedron Lett* **1987**, *28*, 5263-5266.

(11) Rule, M.; Matlin, A.R.; Seeger, D.E.; Hilinski, E.F.; Dougherty, D.A.; Berson, J.A. *Tetrahedron* **1982**, *38*, 787-798.

(12) Recent theoretical work suggests that 2-Me may have pyramidal radical centers, but that inversion via tunneling may be rapid at all temperatures. Pranata, J.P.; Dougherty, D.A. *J Phys Org Chem* , submitted.

(13) See also: Muller, J.-F.; Muller, D.; Dewey, H.J.; Michl, J. *J Am Chem Soc* **1978**, *100*, 1629-1630.

(14) McConnell, H.M. *J Chem Phys* **1960**, *33*, 115-121. Reitz, D.C.; Weissman, S.I. *J Chem Phys* **1960**, *33*, 700-704. Glarum, S.H. Marshall, J.H. *J Chem Phys.* **1967**, *47*, 1374-1378.