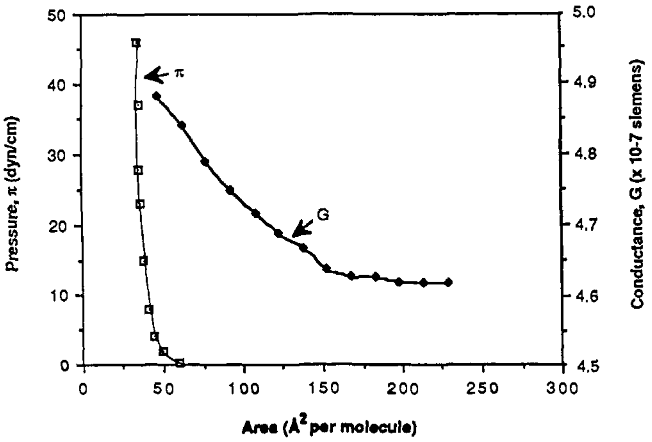

Figure 1. Plots of pressure (π) and conductance (G) vs film area for dipalmitoylphosphatidylethanolamine. Data are taken from Morgan et al.[5]

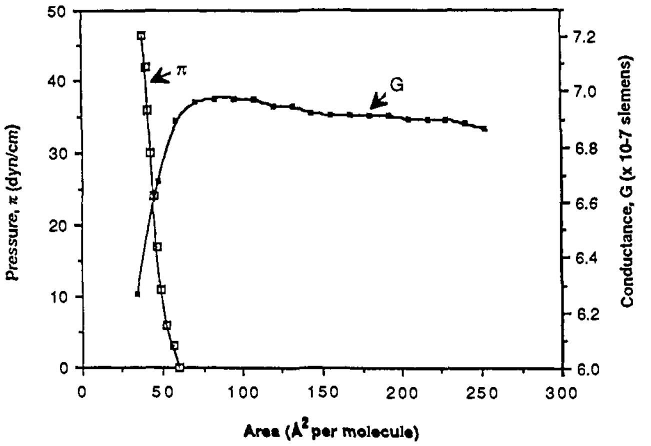

Figure 2. Plots of pressure (π) and conductance (G) vs film area for distearoylphosphatidylcholine at 23.5 °C. Plots were traced simultaneously using ac circuitry for the conductance measurements. Similar curves were obtained in deionized water and 0.5 μM NaCl as the subphase.

ducible electrode immersion depth of 3.0 mm. (c) Applied voltages were adjusted between 1.5 and 20 V to optimize response and stability. (d) A second pair of Pt electrodes was placed in the subphase but outside the film so as to subtract automatically any spurious effects. Yet even with these and other measures, the base lines (i.e., conductance vs area with no film) meandered and, in fact, often resembled the conductance data in Figure 1.

Since polarization effects, exacerbated by dc circuitry,[8] were a possible source of complications, we converted to an ac system (1000 Hz, 1.0 V rms) and thereby secured flat base lines and the data in Figure 2 on DSPC monolayers. Comparison of the pressure/area and conductance/area plots shows that DSPC has little affect on conduction, relative to the base line, until formation of a "condensed" film at high pressures causes the conduction to fall abruptly. Dioctadecyltrimethylammonium bromide monolayers display the same behavior as DSPC, proving that the "condensed film effect" is not specific to zwitterionic lipids. These observations are explainable by lateral ion movement that involves adventitious protons not the monolayer constituents. Protons move rapidly through structured water[9] believed to exist at the water/air interface.[10] This highly conducting water layer could be disrupted and proton transfer impeded, when film pressures of >3 dyn/cm create a close-packed film.

An alternative but reasonable rationale is consistent with Figure 2.[11] The ionic headgroups of a close-packed film might collect ions that normally swim freely in the subphase (similar to the way a micellar surface binds counterions).[12] Conductance would thereby decrease especially if the measurements reflect primarily the properties of the subphase. Although the molecular basis of Figure 2 is still uncertain, the data are noteworthy in showing no observable conductance along monolayers as argued for by Prats[3] and by Morgan[5] over the objections of Gutman.[4]

Several considerations mitigate against yet another explanation of Figure 2, namely that lipid is deposited on the Pt electrodes at high film pressures: (a) Deposition would have to be a highly cooperative phenomenon in order to generate an adsorption isotherm resembling the conductance/area curve in Figure 2. (b) No glitch was observed in the concurrently traced pressure/area plot as might be expected if lipid were being removed from the monolayer during compression. (c) Repeated dippings of clean electrodes through films at high pressure (20 dyn/cm) produced no detectable transfer of lipid. (d) Conductance/area curves are reversible; any binding to the electrodes would require fast desorption processes as the film re-expands.[13]

In summary, we have shown that lipid films at water/air interfaces lack any special propensity to conduct. The data are in conflict with previously published results,[3,5] but, more importantly, they imply that surfaces of biological membranes, in the absence of carriers, serve as poor conduits for ion movement.[14]

Acknowledgment. This work was supported by the Army Research Office and the National Science Foundation.

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[7] Morgan et al.[5] did not protect their system from CO_2 but, instead, allowed the subphase to equilibrate with atmospheric CO_2.

[8] Shoemaker, D. P.; Garland, C. W.; Nibler, J. W. *Experiments in Physical Chemistry*; 5th ed.; McGraw-Hill: New York, 1989; p 256.

[9] Eigen, M. *Angew. Chem. Int., Ed. Engl.* **1964**, *3*, 1.

[10] Fowkes, F. M. *J. Phys. Chem.* **1963**, *67*, 2538.

[11] This was suggested by Professor Robert G. Bergman.

[12] Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111.

[13] Professor Morgan has mentioned (private communication) that our results can be rationalized by a tiny decrease in the meniscus level at high film pressures. Such an effect cannot explain, of course, our flat nonconducting region from 75–250 Å²/molecule where Morgan et al.[5] claim the films conduct.

[14] Recent work has shown that rates of proton transfer in water *decrease* upon addition of 2 M NaCl. Politi, M. J.; Chaimovich, H. to appear in *J. Solution Chem.*

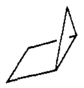
Diphenylbicyclo[2.1.0]pentane. A Persistent Hydrocarbon with a Very Weak C-C Bond

Frank D. Coms[1] and Dennis A. Dougherty*

Contribution No. 7930
Arnold and Mabel Beckman Laboratories of
Chemical Synthesis, 164-30
California Institute of Technology
Pasadena, California 91125

Received March 29, 1989

The bicyclo[2.1.0]pentane structure is unsurpassed among simple ring systems in the amount of strain energy (SE) released upon a single bond homolysis.[2,3] In the parent, **1**, C1–C4 bond cleavage to produce 1,3-cyclopentanediyl **2** relieves ca. 50 kcal/mol of SE.[3] This is manifest in the low barrier for the "bridge-flip" process (Figure 1), for which $\Delta H^{*} = 36.3$ kcal/mol and $\Delta S^{*} = 2.1$ eu.[4] As shown in Figure 1, 36 kcal/mol represents an upper limit to the bond dissociation energy (BDE) in **1**.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2

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[1] JPL-CSMT Fellow, 1987–89.

[2] Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

[3] Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312–322.

[4] (a) Baldwin, J. E.; Ollerenshaw, J. *J. Org. Chem.* **1981**, *46*, 2116–2119. See also: (b) Chesik, J. P. *J. Am. Chem. Soc.* **1962**, *84*, 3250–3253. (c) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1969**, *730*, 82–90.

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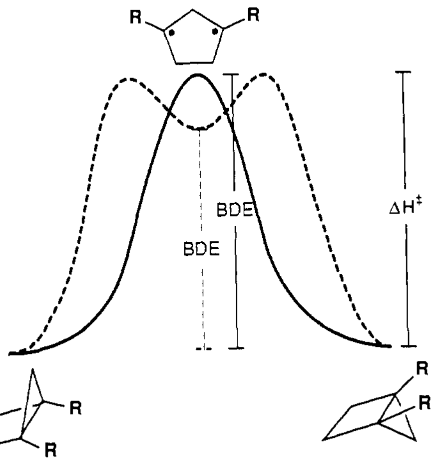
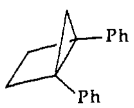


Figure 1. Schematic potential energy surfaces for the bridge-flip of a bicyclo[2.1.0]pentane. As shown, the BDE is less than or equal to $\Delta H^{\ddagger}$, depending on whether there is (dashed line) or is not (solid line) a biradical minimum on the singlet surface.

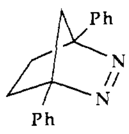
Introduction of phenyl groups at the bridgeheads to produce **3** should preferentially stabilize the derived biradical **4** by ca. 20 kcal/mol due to benzylic resonance.[5] One would expect most or all of this stabilization to be felt in the bridge-flip transition state,[4c] and so diphenylbicyclopentane **3** should have a quite low barrier to bond cleavage. We report herein that for **3**, the bridge-flip barrier—and hence the BDE—is even lower than this reasoning would predict. We put an upper limit of only *12 kcal/mol* on the BDE of **3**. Yet, the molecule is indefinitely long-lived (persistent)[6] at room temperature and above in fluid media.[7]



3

4

Photolysis or gentle heating (35 °C) of diazene **5**[8,9] cleanly produces **3**. Its 20 °C ^{1}H NMR spectrum is shown in Figure 2. The bridge-flip of **3** interconverts exo–endo pairs of protons (Figure 2), and if the barrier were near 16 kcal/mol, it should be observable by dynamic NMR methods. Heating **3** does, in fact, lead to a coalescence of NMR signals (Figure 2), and we have determined rates for this process by complete line shape analysis (CLS).[10] We have also determined bridge-flip rates at lower temperatures using magnetization transfer (MT) technqiues.[10] As in previous studies[12] the rates determined by the two methods lie on the same line in an Eyring plot (Figure 3). The combined methods allow us to span an 84° temperature range and over a factor of 100 in rates, instilling considerable confidence in the derived activation parameters. The values obtained are as follows: $\Delta H^{\ddagger} = 12.2 \pm 0.6$ kcal/mol; $\Delta S^{\ddagger} = -16.4 \pm 1.5$ eu; $\Delta G^{\ddagger}(297) = 17.1 \pm 0.1$ kcal/mol.[13]



5

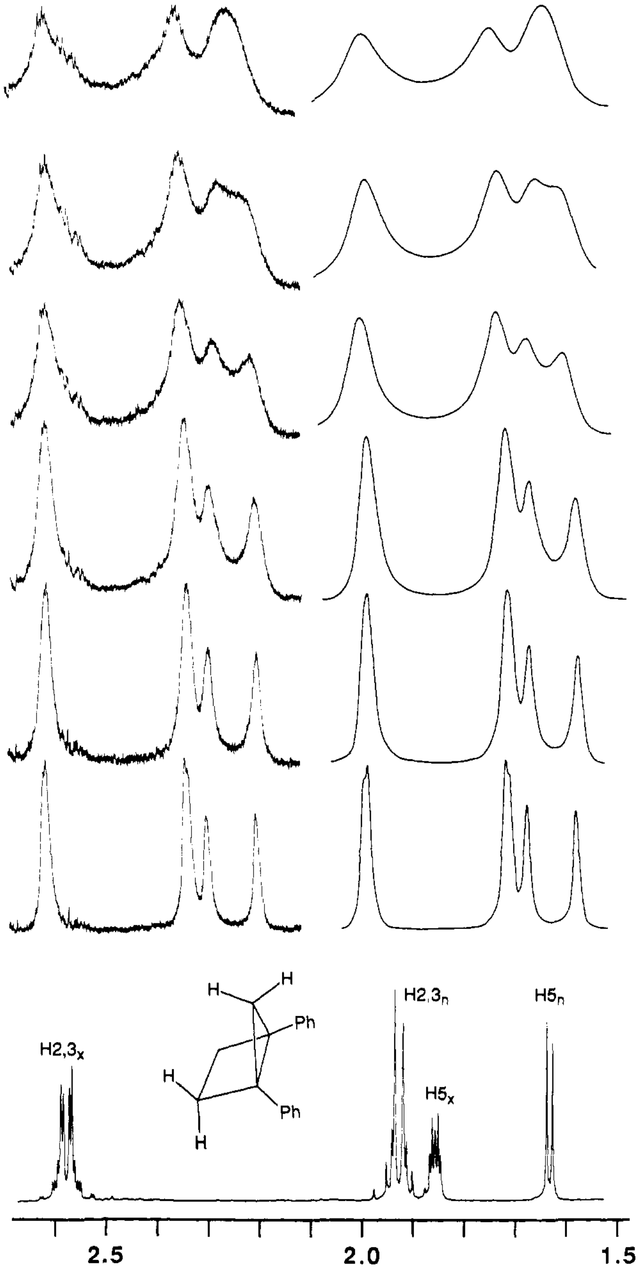


Figure 2. From bottom to top: 400 MHz ^{1}H NMR spectrum (CDCl$_3$; 20 °C) of **3**; observed (left) and simulated (right) spectra at the following temperatures (k in parentheses, s^{-1}): 343.1 K (29 ± 4); 352.9 K (55 ± 5); 363.0 K (90 ± 8); 373.1 K (145 ± 10); 377.6 K (195 ± 10); 382.6 K (250 ± 10). The three highest temperature spectra display increasing amounts of 1,3-diphenylcyclopentene overlapping the H2,3 peaks. MT studies produced the following data: 298.1 K (1.9 ± 0.3); 308.5 K (4.2 ± 0.4); 315.0 K (6.5 ± 0.6).

The 12-kcal/mol bridge-flip barrier is significantly less than the 16 kcal/mol predicted above. This results, at least in part, from ground-state destabilization of **3** due to steric repulsions

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(5) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230–1235.

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

(7) The molecule undergoes a 1,2-hydrogen shift to give 1,3-diphenylcyclopentene beginning at ca. 100 °C. See Figure 2.

(8) Coms, F. D.; Dougherty, D. A. *Tetrahedron Lett.* **1988**, *29*, 3753–3756.

(9) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751–753.

(10) For details of the line shape analysis, magnetization transfer studies, and error analysis, see ref 11. The procedures are similar to those of ref 12b.

(11) Coms, F. D. Ph.D. Thesis, California Institute of Technology, 1989.

(12) (a) Anet, F. A. L.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 760–768. (b) Chang, M. H.; Masek, B. B.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1124–1133.

(13) Several other, more highly substituted, 1,4-diphenylbicyclo[2.1.0]pentanes have been reported to undergo bridge-flip reactions. (See for example: Paquette, L. A.; Leichter, L. M. *J. Am. Chem. Soc.* **1971**, *93*, 5128–5136. Arnold, D. R.; Morchat, R. M. *Can. J. Chem.* **1977**, *55*, 393–406. Wong, P. C.; Arnold, D. R. *Can. J. Chem.* **1979**, *57*, 1037–1049. Brown-Wensley, K. A.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162–4172.) In all cases, however, the reactions are much slower ($\Delta H^{\ddagger} \geq 25$ kcal/mol) than reported here. The greater bond strengths of these compounds may originate from steric constraints which prevent full ultilization of benzyl resonance in the transition state for bond cleavage.

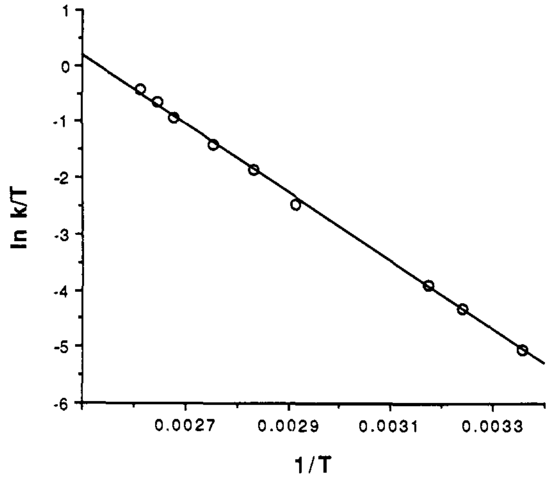

Figure 3. Eyring plot for combined CLS and MT data.

between the phenyls. Simple molecular mechanics calculations[14] suggest that the effect should be worth about 4 kcal/mol, in good agreement with observation. The value of $\Delta S^{\ddagger}$ is also surprisingly low compared to that of the parent system (**1**). We originally thought that this could indicate the triplet **4** (^{3}**4**) is involved. Such reasoning appeared to be supported by the unusually long lifetimes reported for ^{3}**4** under both cryogenic, matrix-isolation,[8] and ambient temperature, fluid-media[9] conditions. However, a survey of the literature reveals a *general* phenomenon wherein diphenyl substitution greatly lowers $\Delta S^{\ddagger}$ values for bond cleavages.[15] There is thus no reason to invoke ^{3}**4**, and we assume that the bridge-flip process is spin conservative.

It seems likely that ^{1}**4** does lie in a potential energy well, and we would estimate its depth at ≤ 5 kcal/mol.[16] Thus, the BDE of **3** (the enthalpy difference between **3** and ^{1}**4**) is 7–12 kcal/mol, in excellent agreement with the 10.9-kcal/mol value determined by Adam and Wirz.[18]

Typically, highly strained molecules are expected to be relatively unstable. Notable exceptions include structures such as cubane[19] and [1.1.1]propellane,[20] for which no one bond homolysis can produce a substantial release of strain. These structures contain no exceptionally weak bonds, by a BDE criterion. Diphenylbicyclopentane is very strained, and the C1–C4 bond is very weak. At room temperature the bond is breaking at a rate greater than 1 s^{-1}, yet **3** is "stable". This is because homolysis produces biradical **4**, which rapidly recloses to **3** before any "detectable" process such as dimerization or 1,2-hydrogen shift can occur.

Molecular oxygen does react with **3** in solution at room temperature. Qualitative kinetic studies show that bond cleavage alone is not rate limiting, i.e., that every ring opening does not lead to trapping. A more detailed analysis of the O_2-trapping reaction is presented in the accompanying manuscript by Adam and Wirz.[18] Their data, combined with that presented here, result in a remarkably detailed model of the kinetic and thermodynamic relationships among **3**, ^{1}**4**, and ^{3}**4**.

Acknowledgment. We thank the National Science Foundation for support of this work. F.D.C. was supported by a Jet Propulsion Laboratory/Center for Space Microelectronics Technology Fellowship sponsored by the Strategic Defense Initiative Organization/Innovative Science and Technology Office. We also thank Professors Adam and Wirz for providing a preprint of ref 9, and for sharing in advance the results of the following manuscript.

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(14) Steric repulsions between the phenyls were estimated by a homodesmotic reaction, in which **1** plus **3** were converted to two molecules of 1-phenylbicyclo[2.1.0]pentane. $\Delta H°$ for this process was calculated to be −4.1 kcal/mol by using MACROMODEL and the standard MM2 force field.

(15) For example, placement of phenyl groups on each end of the cleaving bond of cyclopropane or cyclobutane decreases $\Delta S^{\ddagger}$ of stereomutation by 24 (Rodewald, L. B.; DePuy, C. H. *Tetrahedron Lett.* **1964**, *5*, 2951–2953) and 12 eu (Jones, G., II; Chow, V. L. *J. Org. Chem.* **1974**, *39*, 1447–1448), respectively. For other homolytic bond cleavage reactions that exhibit similar behavior, see: Engel, P. S. *Chem. Rev.* **1980**, *80*, 99–150; and ref 11.

(16) We have previously presented arguments[17] that singlet 1,3-biradicals with delocalizing substituents will most likely lie in a well. The 5 kcal/mol upper limit derives from two observations. First, our qualitative observations[8] on the matrix decay of ^{3}**4** suggest a barrier on the order of 4 kcal/mol, and since the singlet–triplet gap is certainly small,[17] the ^{1}**4** barrier cannot be much larger. Second, if the barrier is >5 kcal/mol, ^{1}**4** should be observable by flash photolysis, but it is not.[9]

(17) Sponsler, M. B.; Jain, R.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 2240–2252.

(18) Adam, W.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.*, following paper in this issue.

(19) Eaton, P. E.; Cole, T. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 3157–3158.

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Oxygen Trapping and Thermochemistry of a Hydrocarbon Singlet Biradical: 1,3-Diphenylcyclopentane-1,3-diyl

Waldemar Adam* and Herbert Platsch

Institut für Organische Chemie
der Universität Würzburg
Am Hubland, D-8700 Würzburg, FRG

Jakob Wirz*

Institut für Physikalische Chemie
der Universität Basel
Klingelbergstrasse 80, CH-4056 Basel, Switzerland

Received April 10, 1989

Our knowledge of absolute rate constants for the reactions of triplet biradical intermediates in solution is rapidly increasing and, as a result, useful structure–reactivity relationships are emerging.[1] In contrast, very little is known about singlet biradicals; recent ab initio calculations[2] for trimethylene and tetramethylene have substantiated the twixtyl hypothesis of a shallow, entropy-dominated free-energy minimum proposed 20 years ago by Hoffmann and co-workers.[3] In particular, the question whether or not singlet 1,3-cyclopentanediyl represents a secondary minimum on the energy surface has been the subject of continuous debate.[4] We now present evidence for diffusional trapping of singlet 1,3-diphenylcyclopentane-1,3-diyl (S).

Triplet 1,3-diphenylcyclopentane-1,3-diyl (T) is remarkably persistent. Its lifetime amounts to ca. 25 μs at room temperature in solution.[5] Coms and Dougherty have observed the ESR spectrum of T with a half-life of hours at 77 K in 2-methyltetrahydrofuran glass; the ESR signal did not disappear upon cooling to 3.8 K, indicating that the biradical has a triplet ground state.[6]

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(1) (a) Wilson, R. M. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1985; Vol. 7, Chapter 5. (b) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521. (c) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* Submitted for publication. (d) Caldwell, R. A. In *Kinetics and Spectroscopy of Biradicals and Carbenes*; Platz, M. S., Ed.; Plenum Publishing Co.: New York, in press.

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(5) Adam, W.; Grabowski, S.; Platsch, H.; Hannemann, K.; Wirz, J.; Wilson, R. M. *J. Am. Chem. Soc.* **1989**, *111*, 751.

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