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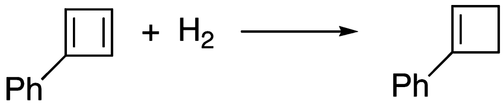

$$\Delta H^\circ_{hyd} = 57.4 \pm 4.9 \text{ kcal mol}^{-1}$$
$$= 62.1 \text{ (G3), } 60.5 \text{ (G3(MP2)), } 59.0 \text{ (B3LYP)}$$

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Experimental Determination of the Heat of Hydrogenation of Phenylcyclobutadiene

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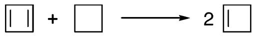
Abstract: The heat of hydrogenation of phenylcyclobutadiene ($\Delta H^\circ_{hyd} = 57.4 \pm 4.9$ kcal mol^{-1}) was determined via a thermodynamic cycle by carrying out gas-phase measurements on 1-phenylcyclobuten-3-yl cation. This leads to an antiaromatic destabilization energy of 27 ± 5 kcal mol^{-1}, a difference of 9.6 ± 4.9 kcal mol^{-1} for the first and second C−H bond dissociation energies of 1-phenylcyclobutene, and an estimate of 96 ± 5 kcal mol^{-1} for the heat of formation of cyclobutadiene. These results are compared to G3, G3(MP2), and B3LYP computations and represent the first experimental measurements of the energy of a monocyclic cyclobutadiene.

Introduction

Cyclobutadiene (**1**) occupies an important place in chemistry and has been the subject of extensive experimental efforts for over 100 years.[1−3] Numerous accomplishments relating to its preparation, characterization, and antiaromatic nature have been reported including matrix-isolated infrared spectra at 8 and 20 K,[4−9] the synthesis and isolation of tetra-*tert*-butylcyclobutadiene (and its corresponding tetrahedrane),[10,11] and the formation of a room-temperature stable molecule containing **1** encapsulated in a polyether cage.[12] As a result of all of this work, it is well-known now that cyclobutadiene has a rectangular D_{2h} geometry and a singlet ground state, and is extremely reactive bimolecularly. Quantitative data addressing the stability or lack thereof of this 4π-electron annulene, however, is largely lacking and has led to controversy regarding its heat of formation,[13,14] relative vs absolute antiaromaticity,[15] and the origin of its instability (i.e. σ vs π framework).[16−19]

A wide variety of computational methods have been employed to address the energetics of cyclobutadiene.[16−36] Simple Hückel calculations indicate that **1** has no π-electron delocalization energy and is less stable than 1,3-butadiene, its acyclic analogue. More sophisticated semiempirical, ab initio, and density functional theory results lead to a heat of formation spanning from 87 (BLYP/6-311G(2d,2p)) to 124 (HF/4-31G) kcal mol^{-1}. If only the most reliable ab initio methodologies are considered (G2, CBS-Q, and CCSD(T)), then this range narrows to 99−104 kcal mol^{-1}. These latter predictions also lead to an antiaromatic destabilization energy (ADE), as given by the reaction in eq 1, of 31−36 kcal mol^{-1}.



(1)

1

ADE = $-\Delta H^\circ_{rxn}$

In contrast, a recent photoacoustic calorimetry study was reported which provided the heat of reaction for the photo-

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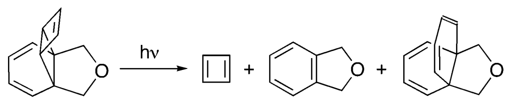
chemically induced conversion of the tetracyclic propellane **2** into cyclobutadiene, phthalene (**3**), and tricyclic tetraene **4** (eq 2).[14]



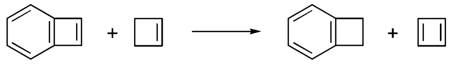
(2)

2 **3** **4**

33% 33% 34%

If the heats of formation of **2**, **3**, and **4** were known, the heat of formation of cyclobutadiene readily could have been obtained from this result. Unfortunately, they have not been determined, so they were estimated using computed molecular mechanics (MM3) geometries and semiempirical AM1 energies. This led Deniz, Peters, and Snyder to report a heat of formation for cyclobutadiene of 114 ± 11 kcal mol^{-1} and an ADE of 46 kcal mol^{-1}; these values are 10−15 kcal mol^{-1} larger than the most sophisticated computational predictions to date.

More recently, Broadus and Kass measured the heat of formation of benzocyclobutadiene (**5**) in the gas phase using a negative-ion thermodynamic cycle.[13] By comparing it to **1** via a homodesmotic reaction (eq 3),[37,38]



(3)

5

MP2 and B3LYP calculations led to ΔH°_f (**1**) = 101 and 103 kcal mol^{-1}, respectively. This is in accord with high-level calculations, but to establish the heat of formation of cyclobutadiene and its ADE, experimental data are needed. We now describe the culmination of an earlier study on the C3−H bond dissociation energy (BDE) of 1-phenylcyclobutene[39] and report the gaseous heat of hydrogenation of phenylcyclobutadiene by employing a positive-ion thermodynamic cycle. Our results are compared to G3 theory predictions, and the effect of the phenyl substituent on cyclobutadiene is estimated.

Experimental Section

General. 3-Phenyl-2-cyclobuten-1-one was prepared and purified by vacuum sublimation as described in the literature.[40−42] Reduction of the ketone to the desired alcohol (**6**) was carried out using a procedure similar to that for the preparation of (4′-carbomethoxymethyl)-3-phenyl-2-cyclobuten-1-ol rather than the one reported for **6**.[43] Solvents were dried by standard methods, and reagents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VAC-300 spectrometer and are reported in parts per million (δ).

3-Phenyl-2-cyclobuten-1-ol (6). To a stirred solution of 0.31 g (2.15 mmol) of freshly sublimed 3-phenyl-2-cyclobuten-1-one in 12 mL of methanol was added 0.51 g of $CeCl_3\cdot 7H_2O$. After cooling to 0 °C, 0.083 g (2.15 mmol) of sodium borohydride was added in small portions over 5 min, and the temperature was maintained for an additional 10 min. Removal of the solvent under reduced pressure afforded a precipitate which was suspended in CH_2Cl_2 and purified by flash chromatography on a short (~15 cm) silica gel column first using CH_2Cl_2 and then 50% more of 15% EtOAc in CH_2Cl_2. White crystals of 3-phenyl-2-cyclobuten-1-ol were obtained (0.30 g, 96%) and can be stored in the dark at −20 °C for at least 3 months without any noticeable decomposition. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (br s, 1H), 2.63 (dt, 1H, J = 12.9 and 1.2 Hz), 3.20 (ddd, 1H, J = 12.9, 3.9, and 0.9 Hz), 4.80 (dt, 1H, J = 3.9 and 0.9 Hz), 6.40 (q, 1H, J = 0.9 Hz), 7.33−7.43 (m, 5H). This compares favorably to the literature spectrum recorded at 60 MHz (i.e. 2.55 (dt, 1H, J = 13.0 and 1.2 Hz), 2.66 (d, OH, J = 7.6 Hz), 3.15 (dq, 1H, J = 13.0, 3.8, and 0.8 Hz), 4.84 (broad, 1H), 6.34 (dt, 1H), 7.33 (5H)).[42] ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 40.5, 67.3, 125.5, 128.5, 128.8, 129.5, 134.0, 147.2.

Gas-Phase Experiments. A dual cell model 2001 Finnigan Fourier transform mass spectrometer (FTMS) equipped with a 3 T superconducting magnet and controlled by an Ion Spec data system running *IonSpec99*, ver. 7.0, was used for these studies. 3-Phenyl-2-cyclobuten-1-ol was added into the first (analyzer) cell at a static pressure of $\sim 4 \times 10^{-8}$ Torr and ionized with 50 eV electrons for 40 ms to afford positive ions at m/z 147 (M + H, ~5%), 146 (M, ~15%), 145 (M − H, ~55%), and 129 (M + H − H_2O, ~25%). The ion of interest (m/z 129 or 147) was transferred to the second (source) cell where it was collisionally cooled with up to three pulses of argon, each leading to pressures of $\sim 10^{-5}$ Torr, and then it was re-isolated using a series of chirp and stored waveform inverse Fourier transform (SWIFT) excitations.[44,45] Neutral reagents were introduced into the source cell via slow leak valves, and the formation of product ions were monitored as a function of time. In this work reported reaction rates are estimated to have an uncertainty of ± 50%.

To probe the structure of the 1-phenylcyclobuten-3-yl cation (**7**), it was reacted with a static pressure of H_2O ($\sim 4 \times 10^{-8}$ Torr) in the analyzer cell. The resulting m/z 147 ion or the one produced by chemical ionization of 3-phenyl-2-cyclobuten-1-ol was transferred to the source cell and bracketed with standard reference bases or fragmented via energetic collisions using sustained off-resonance irradiation (SORI).

Computations. Calculations were carried out using *Gaussian 2003*[46] on IBM and SGI workstations at the Minnesota Supercomputer Institute. Density functional theory optimizations and vibrational frequencies were computed using the Becke three-parameter hybrid exchange[47] and Lee−Yang−Parr[48] correlation density functional (R(U)B3LYP) with the 6-31G(d) and 6-31+G(d) basis sets, and single-point energies were obtained with the aug-cc-pvtz basis set.[49] Since the 6-31+G(d) energies agree with

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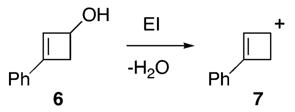
those obtained using the larger aug-cc-pvtz basis set to within 1.0 kcal mol^{-1} on average, only the former data are given in the text. G3 and G3(MP2) energies also are reported and were obtained as previously described.[50,51] All of the resulting thermodynamic quantities were corrected to 298 K using unscaled B3LYP or scaled (0.8929) HF frequencies.

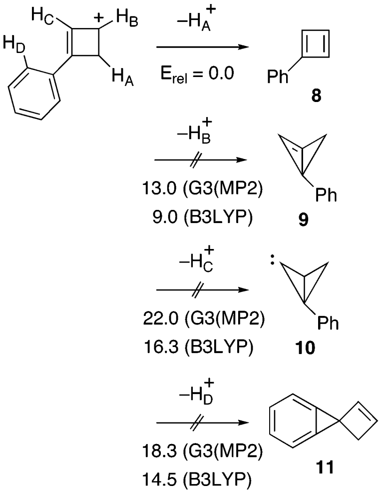
Results/Discussion

Structural Authentication. Electron ionization of a static pressure of 3-phenyl-2-cyclobuten-1-ol (**6**) leads to 1-phenylcyclobuten-3-yl cation (**7**, *m*/*z* 129, ~25%) among other ions presumably via fragmentation of the M and M + H ions (eq 4).



(4)

The identity of this substituted 1-phenylallyl cation was not in doubt since it is stabilized by the phenyl group and has no apparent low-energy rearrangement pathway available and our thermodynamic measurements are reproduced by high-level computations; the acidity also is structurally diagnostic (see below). Nevertheless, we probed this species further by reacting it with water and examining the resulting adduct in comparison to the independently prepared ion formed by self-chemical ionization of **6**. In both cases, the resulting $C_{10}H_{11}O^+$ ion (*m*/*z* 147) protonates *N*,*N*-diethylhydroxylamine (Et_2NOH, PA = 218.6 ± 2.0 kcal mol^{-1}) and aniline ($PhNH_2$, PA = 210.9 ± 2.0 kcal mol^{-1}) but not pyrrole (PA = 209.2 ± 2.0 kcal mol^{-1}), ammonia-d_3 (PA = 204.0 ± 2.0 kcal mol^{-1}), and weaker bases.[52] One H−D exchange is observed with ND_3 and the rate constant for the disappearance of the d_0 species is (6.6 ± 1.0) × 10^{-10} cm^3 molecule^{-1} s^{-1}. Likewise, sustained off-resonance irradiation (SORI) collision-induced dissociation (CID) leads to ions at *m*/*z* 129 (M − H_2O, ~45%), 128 (M − H_3O, ~10%), 91 (M − C_3H_4O, ~10%) and 69 (M − C_6H_6, ~35%) regardless of how the *m*/*z* 147 ion is produced.[53] These results indicate that both **6** and **7** lead to the same species.



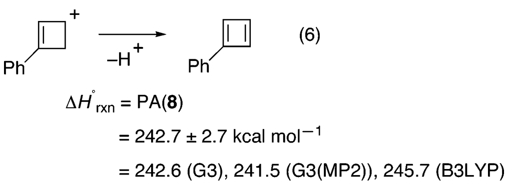
(5a)
(5b)
(5c)
(5d)

Bracketing Experiments. Deprotonation of 1-phenylcyclobuten-3-yl cation affords phenylcyclobutadiene (**8**) because a π bond is formed and the energetic benefit (~60 kcal mol^{-1}) outweighs the antiaromatic destabilization of the system (~30 kcal mol^{-1}, see below). The latter interaction, however, decreases the acidity of **7** so that a large numerical value for the proton affinity of **8** is expected. Additional deprotonation products can be envisioned (eq 5), but the corresponding carbene (**9**, $-H_B$), allene (**10**, $-H_C$), and benzocyclopropene (**11**, $-H_D$) would seem to be much less stable; **9** and **10**, as previously noted, are best described as 3-phenylbicyclo[1.1.0]but-1(2)-ene and 1-phenyl-2-bicyclo[1.1.0]butylidene and are illustrated as such.[54,55] To test this expectation, G3(MP2) and B3LYP calculations were carried out, and phenylcyclobutadiene is found to be significantly more stable than the other isomers. Consequently, the acidity of 1-phenylcyclobuten-3-yl cation was measured by reacting it with standard reference bases and observing the occurrence or nonoccurrence of proton transfer (Table 1). Strong bases such as pyrrolidine, diisopropylamine, and 1,4-butanediamine do not abstract a proton from **7**, whereas the more basic 3-(dimethylamino)propylamine does with a rate constant of 3.5 × 10^{-10} cm^3 molecule^{-1} s^{-1}. These observations enable us to assign PA(**8**) = 242.7 ± 2.7 kcal mol^{-1}, which is a much larger value than that measured for any other hydrocarbon and is in excellent accord with computed results of 242.6 (G3), 241.5 (G3(MP2)), and 245.7 (B3LYP) kcal mol^{-1} (eq 6).[56]

Table 1. Proton Affinity Measurement Results for Phenylcyclobutadiene (**8**)

cmpd	ΔH°_{acid} (kcal mol^{-1})	proton transfer
ammonia-d_3	204.0 ± 2.0[a]	no
pyrrolidine	226.6 ± 2.0	no
diisopropylamine	232.3 ± 2.0	no
1,3-propanediamine	235.9 ± 2.0	no
1,4-butanediamine	240.3 ± 2.0	no[b]
3-(dimethylamino)propylamine	245.0 ± 2.0	yes[c]

[a] This value is for NH_3. [b] An adduct - NH_3 at *m*/*z* 200 was observed. [c] k = 3.5 × 10^{-10} cm^3 molecule^{-1} s^{-1}.



$$\Delta H^\circ_{rxn} = PA(\mathbf{8})$$
$$= 242.7 \pm 2.7\ \text{kcal mol}^{-1}$$
$$= 242.6\ (G3),\ 241.5\ (G3(MP2)),\ 245.7\ (B3LYP)$$

The ionization potential of 1-phenylcyclobuten-3-yl radical (**7r**) also was measured by bracketing (Table 2). In particular, tetraethylhydrazine (Et_2NNEt_2) and species with higher ionization potentials do not undergo electron transfer with **7r**, whereas

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(53) Exact mass measurements were made to verify the elemental composition of the fragment ions.

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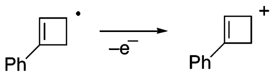
(56) B3LYP computations for the proton affinity of cyclobutadiene decrease by 4.9 kcal mol^{-1} when diffuse functions are included in the 6-31G(d) basis set, but the value is still 5.7 kcal mol^{-1} larger than that predicted using G3 theory. Using the larger aug-cc-pvtz basis set further reduces this difference but by only 1.2 kcal mol^{-1}, so we have empirically corrected the B3LYP/6-31+G(d) energy by 5.7 kcal mol^{-1}.

Table 2. Ionization Potential Bracketing Results for 1-Phenylcyclobutenyl Radical (**7r**)

cmpd	IP (eV)	electron transfer
N,*N*-diethylaniline	6.98 ± 0.05	no[a]
N-phenylpyrrolidine	6.80 ± 0.02	no[a]
tetraethylhydrazine	6.50 ± 0.05	no[a]
dicyclopentadienylnickel	6.24 ± 0.07	yes[b]

[a] Adduct formation was observed. [b] $k = 1.9 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

dicyclopentadienylnickel (Cp_2Ni) donates an electron efficiently ($k = 1.9 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}). This leads to IP(**7r**) = 6.37 ± 0.14 eV or 146.9 ± 3.2 kcal mol^{-1}, which is in reasonable accord with computed values of 6.57 (G3), 6.50 (G3-(MP2)), and 6.44 (B3LYP) eV (eq 7).

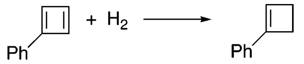


(7)

7r

$$\Delta H^{\circ}_{rxn} = \mathrm{IP}(\mathbf{7r})$$
$$= 146.9 \pm 3.2 \text{ kcal mol}^{-1}$$
$$= 151.5 \text{ (G3)}, 150.0 \text{ (G3(MP2))}, 148.6 \text{ (B3LYP)}$$

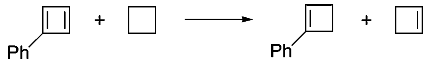
Thermochemistry. By combining our measurements for the proton affinity of phenylcyclobutadiene and the ionization potential of 1-phenylcyclobuten-3-yl radical with the recently determined allylic C3−H bond dissociation energy of 1-phenylcyclobutene (85.6 ± 2.6 kcal mol^{-1})[39] and the well-known values for the ionization energy of the hydrogen atom (313.6 kcal mol^{-1}) and the bond energy of molecular hydrogen (104.2 kcal mol^{-1}), one can obtain an experimentally determined heat of hydrogenation for **8** of 57.4 ± 4.9 kcal mol^{-1} (eq 8).



(8)

$$\Delta H^{\circ}_{hyd} = -\Delta H^{\circ}_{rxn}$$
$$= 57.4 \pm 4.9 \text{ kcal mol}^{-1}$$
$$= 62.1 \text{ (G3)}, 60.5 \text{ (G3(MP2))}, 59.0 \text{ (B3LYP)}$$

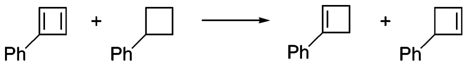
This compares favorably with predicted values of 62.1 (G3), 60.5 (G3(MP2)), and 59.0 (B3LYP) kcal mol^{-1},[56] but is more than double the value for 1-phenylcyclobutene ($\Delta H^{\circ}_{hyd} = 26.8$ kcal mol^{-1})[57] and almost twice the value for cyclobutene ($\Delta H^{\circ}_{hyd} = 30.7 \pm 0.4$ kcal mol^{-1}).[58] These large differences are a reflection of the antiaromatic destabilization energy of phenylcyclobutadiene, which is 26.7 ± 4.9 kcal mol^{-1} as given by eq 9.



(9)

$$-\Delta H^{\circ}_{rxn} = 26.7 \pm 4.9 \text{ kcal mol}^{-1}$$
$$= 29.8 \text{ (G3)}, 29.5 \text{ (G3(MP2))}, 32.2 \text{ (B3LYP)}$$

Alternatively, one can use the reaction illustrated in eq 10, but the same result is obtained because the phenyl substituent on cyclobutane and at the 3-position of cyclobutene effectively cancel each other.



(10)

$$-\Delta H^{\circ}_{rxn} = 29.6 \text{ (G3)}, 29.3 \text{ (G3(MP2))}, 32.0 \text{ (B3LYP)}$$

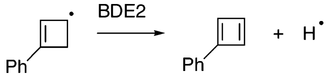
Table 3. Experimental and Computed Heats of Formation

	ΔH°_f (kcal mol^{-1})			
cmpd	Benson's method[a]	G3(MP2)[b]	G3[b]	expt
cyclobutane	6.8	7.1	7.1	6.78 ± 0.14[c]
cyclobutene	37.3	39.2	39.9	37.45 ± 0.37[c]
cyclobutadiene		102.2	103.9	
phenylcyclobutane	32.8	29.5	31.1	
1-phenylcyclobutene	59.6	56.8	58.9	
3-phenylcyclobutene	63.1	61.8	64.1	
phenylcyclobutadiene		118.4	121.5	116 ± 6[d]

[a] See ref 53. [b] Computed via atomization energies. [c] See ref 54. [d] Based upon the measured heat of hydrogenation and an estimated heat of formation for 1-phenylcyclobutene of 59 ± 3 kcal mol^{-1}, where the given uncertainty represents a conservative estimate.

The heat of formation of phenylcyclobutadiene can be derived from our data if the heat of formation of 1-phenylcyclobutene is available. Unfortunately, this quantity has not been measured, so we estimated it using Benson's group equivalents method[57] and computed G3 and G3(MP2) atomization energies (Table 3). If the average of the first two approaches is used (59 ± 3 kcal mol^{-1}), then ΔH°_f (**8**) = 116 ± 6 kcal mol^{-1} is obtained. This can be equated to the sum of the Benson strain-free energy components (51.2 kcal mol^{-1}), the strain energy, and the antiaromatic destabilization energy. A value of 32.8 kcal mol^{-1} has been used for the SE of cyclobutadiene (this corresponds to the strain for cyclobutane and an additional 1.5 kcal mol^{-1} per sp^2-hybridized carbon)[14] and leads to an ADE of 32 kcal mol^{-1}, which is in reasonable accord with the other predictions of this quantity.

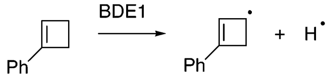
Our PA and IE measurements (eqs 6 and 7) enable us to derive the C−H bond strength of 1-phenylcyclobuten-3-yl radical (eq 11, BDE2 = 76.0 ± 4.2 kcal mol^{-1}) and compare it to the allylic C3−H BDE of 1-phenylcyclobutene (eq 12, BDE1 = 85.6 ± 2.6 kcal mol^{-1}).[59]



(11)

76.0 ± 4.2 kcal mol^{-1}

80.0 (G3), 77.2 (G3(MP2)), 81.0 (B3LYP)



(12)

85.6 ± 2.6 kcal mol^{-1}

88.0 (G3), 89.8 (G3(MP2)), 83.5 (B3LYP)

The difference is a mere 9.6 ± 4.9 kcal mol^{-1} as compared to 66 ± 1 kcal mol^{-1} for ethane and 61 ± 1 kcal mol^{-1} for cyclobutane. This disparity is due in large part to the reduced value for BDE1 because of the additional stability of the resulting allylic radical. If one attempts to correct for this by using model compounds such as ethylbenzene and cyclopentene (BDE1 − BDE2 = 38.4 ± 2.1 and 36.7 ± 1.4 kcal mol^{-1}, respectively), then the gap is reduced, and the remaining difference of ~28 kcal mol^{-1} can be attributed to the ADE. In

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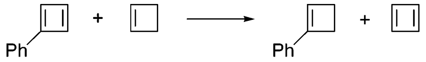
(57) This quantity was obtained using Benson's group equivalents approach. Cohen, N.; Benson, S. *Chem. Rev.* **1993**, *93*, 2419−2438.

(58) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970; pp 1−643.

(59) The B3LYP value for BDE2 has been corrected for the apparent error in the computed energy of phenycyclobutadiene as indicated in ref 56.

any case, the BDE1 − BDE2 difference indicates that phenylcyclobutadiene is an excellent radical trap from a thermodynamic perspective and does not provide a good measure of the strength of its second π bond; a better estimate for the π bond strength is 34 kcal mol^{-1} (the π bond strength for cyclobutene + $\Delta H^\circ_{\mathrm{rxn}}$ (eq 9)).

A natural question to ask at this point is what effect does the phenyl group have on the stability of cyclobutadiene? This question can be answered by comparing the heats of hydrogenation of **1** and **8** as illustrated in eq 13.



(13)

$$\Delta H^\circ_{\mathrm{rxn}} = \Delta H^\circ_{\mathrm{hyd}}(\mathbf{1}) - \Delta H^\circ_{\mathrm{hyd}}(\mathbf{8})$$
$$= 1.4\ (\mathrm{G3}),\ 1.4\ (\mathrm{G3(MP2)}),\ 2.8\ (\mathrm{B3LYP})$$

Homodesmotic reactions such as this one should be reliably reproduced at a variety of computational levels since electron correlation effects largely cancel each other, and indeed, diverse methods such as HF, MP2, MP3, MP4, QCISD(T), G3(MP2), and G3 all predict that this transformation is slightly endothermic (i.e. the values range from 1.1 to 2.0 kcal mol^{-1}). In other words, the heat of hydrogenation of cyclobutadiene is ~2 kcal mol^{-1} larger than that for phenylcyclobutadiene, presumably because of the additional conjugation in the latter species. If we combine the G3 prediction with our experimental value for $\Delta H^\circ_{\mathrm{hyd}}$ (**8**), then $\Delta H^\circ_{\mathrm{hyd}}$ (**1**) = 59 ± 5 kcal mol^{-1} is obtained[60] and $\Delta H^\circ_{\mathrm{f}}$ (**1**) = 96 ± 5 kcal mol^{-1} can be derived on the basis of the experimental heat of formation of cyclobutene (37.45 ± 0.37 kcal mol^{-1}); $\Delta H^\circ_{\mathrm{f}}$ (**1**) = 99 kcal mol^{-1} is obtained if the G3 heat of formation for cyclobutene obtained via its atomization energy is used. This result is on the low side of recent predictions; therefore, we also computed the heat of formation of cyclobutadiene via its atomization energy, heat of hydrogenation, and homodesmotic reaction with cyclobutane (i.e., eq 1). These results are summarized in Table 4 and lead us to predict that 96 ≤ $\Delta H^\circ_{\mathrm{f}}$ (**1**) ≤ 104 kcal mol^{-1} or that the heat of formation is ~100 kcal mol^{-1}. This finding is consistent with our previous estimate of 102 kcal mol^{-1} but is much smaller than the value of 114 kcal mol^{-1} reported by Deniz, Peters, and Snyder, in part because of the computational approach they used.[14] More sophisticated MP2 or DFT calculations were found to lower the heat of formation by ~4 kcal mol^{-1}.[61]

Table 4. Predicted Heat of Formation of Cyclobutadiene

rxn	$\Delta H^\circ_{\mathrm{f}}$ (kcal mol^{-1}) B3LYP	G3(MP2)	G3
atomization		102.2	103.9
hydrogenation	105.0	99.4	101.0
equation 1	103.8	99.0	99.3
avg (± std dev)	104.4 ± 0.8	100.2 ± 1.7	101.4 ± 2.3

Conclusions

The gas-phase heat of hydrogenation for phenylcyclobutadiene has been experimentally determined via a thermodynamic cycle by making measurements on 1-phenylcyclobuten-3-yl cation. This enables a wealth of thermochemical data to be derived, including the antiaromatic destabilization energy, a comparison of the first and second C−H bond energies of 1-phenylcyclobutene, and an estimate of the heat of formation of phenylcyclobutadiene based upon the prediction of the heat of formation of 1-phenylcyclobutene. Interestingly, phenylcyclobutadiene is found to be a remarkably good radical trap from an energetic perspective because the antiaromaticity of the ground state is relieved and the 1-phenylallyl radical produced is stabilized by delocalization. Our results also suggest that the parent compound is significantly more stable than the only "experimental" determination reported to date.

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Supporting Information Available: Computed structures and energies; complete ref 46. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0525511

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(60) We assumed that the G3 reaction energy has an uncertainty of ±2 kcal mol^{-1}.

(61) Glasovac, Z.; Eckert-Maksic, M.; Kass, S. R. Unpublished results.