

Extraordinary Large Stabilization of the Phenyl Cation by Hyperconjugation with Strained Bonds. Experimental Confirmation of a Theoretical Prediction

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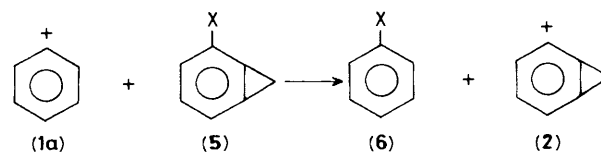
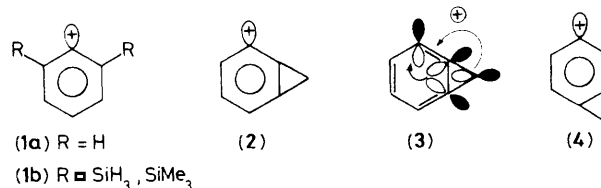
Appearance energy measurements for the loss of Br[•] from ionized 2-bromocyclopropabenzene (**5c**), in conjunction with thermochemical data, suggest that the 2-cyclopropaphenyl cation (**2**) is stabilized, relative to the phenyl cation (**1a**), by at least 27.6 kcal/mol, in very good agreement with a previous prediction based on *ab initio* MO calculations (≥ 23 kcal/mol at 3-21G*); the heat of formation of (**2**) is estimated to be 311 kcal/mol (1 cal = 4.184 J).

Hyperconjugation between the empty 2p(C⁺) orbital and suitable β -C-R bonds is the key to the stabilization of the elusive phenyl cation (**1a**) (R = H) which was at the focus of numerous previous investigations.^{1,2} The theoretical prediction by Apeloig and Arad¹ that the introduction of two silyl-substituents at the 2,6-positions would stabilize the aryl cations (**1b**) to such an extent that they will become viable transients under solvolysis conditions has recently been confirmed by Sonoda *et al.*² These authors demonstrated that in trifluoroethanol the solvolysis of 2,6-bis(trimethylsilyl)-phenyl trifluoromethanesulphonate indeed proceeds *via* an aryl cation intermediate (**1b**) (R = SiMe₃).²

Alternatively, it was suggested¹ that the phenyl cation can be stabilized through hyperconjugation with high-lying strained carbon-carbon bonds,³ as in the cyclopropabenzene derivative (**2**). The major stabilizing interaction in this case, that between the empty 2p(C⁺) orbital and the highest occupied Walsh orbital of the fused cyclopropene ring, is shown schematically in (**3**). The resulting stabilization is indeed very large. According to *ab initio* MO calculations (**2**) is more stable than (**1a**) by 23 kcal/mol (3-21G*) (1 cal = 4.184 J).¹ Similarly, (**2**) is more stable by 22 kcal/mol (3-21G*) than its *meta*-isomer (**4**), where hyperconjugation with the cyclopropene ring cannot take place. The inclusion in the calculations of electron correlation effects, which is prohibited by the size of the system, was predicted to stabilize (**2**) relative to (**1a**) even further.¹ We report here experimental data which for the first time confirms quantitatively this theoretical prediction.

Straightforward arguments demonstrate that the stabilization energy (S.E.) of cation (**2**) relative to cation (**1a**), as derived from the isodesmic⁴ equation in Scheme 1, can be expressed by the difference in the appearance energies (A.E.) of the cations (**1a**) and (**2**) from their respective precursors (**6**) and (**5**) (equation 1).

$$\text{S.E.}(\mathbf{2}) = \text{A.E.}(\mathbf{2}) - \text{A.E.}(\mathbf{1a}) \quad (1)$$



a; X = H
b; X = Cl
c; X = Br

Scheme 1

The appearance energy of cation (2) from (5c)⁵ [*i.e.*, for the fragmentation reaction (5c) → C₇H₅⁺ + Br[•]] was measured to be 10.5 ± 0.1 eV.† The use of this value together with the well-established appearance energy of 11.7 eV⁶ for (1a) from bromobenzene (6a), results (using equation 1) in a stabilization energy of (2) which is larger than 27.6 kcal/mol.‡ This measured value is in very good agreement with the theoretical prediction¹ (calculated using the equation in Scheme 1) that S.E.(2) is in excess of 23 kcal/mol.

Using an appropriate thermochemical cycle the heat of formation, ΔH_f^o, of (2) can be calculated from equation (2). The heat of formation of (1a) is now generally agreed upon to be 270 kcal/mol,^{6,7} but the heat of formation of (5c) is unknown. However, the difference in the heats of formation of the corresponding hydrocarbons (6a) and (5a) is known experimentally⁸ or predicted theoretically⁹ to be of the order of 67–70 kcal/mol. Assuming that a similar difference holds also for the corresponding bromides (5c)–(6c),§ we arrive at an estimate for ΔH_f^o(2) of 311 kcal/mol.

$$\Delta H_f^o(2) = \Delta H_f^o(1a) + A.E.(2) - A.E.(1a) + \Delta H_f^o(5) - \Delta H_f^o(6) \quad (2)$$

The ionization energy (I.E.) of (5c) was determined to be 10.1 ± 0.1 eV, practically identical with I.E.(5a) = 10.17 eV obtained earlier by Heilbronner *et al.*¹⁰ using photoelectron spectroscopy. This similarity suggests that in both (5a) and

(5c) ionization occurs from a π-type benzene orbital of b₁ symmetry.⁹

Experiments aimed at generating by solvolysis the 2-cyclopropaphenyl cation (2) and related species are in progress.

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References

- 1 Y. Apeloig and D. Arad, *J. Am. Chem. Soc.*, 1985, **107**, 5285, and references cited therein.
- 2 Y. Himeshima, H. Kobayashi, and T. Sonoda, *J. Am. Chem. Soc.*, 1985, **107**, 5286.
- 3 R. Gleiter, *Top. Curr. Chem.*, 1979, **86**, 197; R. Gleiter, G. Jahne, M. Oda, and M. Iyoda, *J. Org. Chem.*, 1985, **50**, 678; A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 809; Z. Rappoport, 'The Chemistry of the Cyclopropyl Group,' chapters by K. B. Wiberg, E. Ballard, and E. C. Friedrich, Wiley, Chichester, 1987.
- 4 For a general discussion, see: W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, 'Ab Initio Molecular Orbital Theory,' Wiley–Interscience, New York, 1986.
- 5 B. Halton and C. J. Randall, *Tetrahedron Lett.*, 1982, 5591; B. Halton, C. J. Randall, G. J. Gainsford, and W. T. Robinson, *Aust. J. Chem.*, 1987, **40**, 475; D. Arad, Ph.D. Thesis, Technion, 1986.
- 6 Y. Malinovich, R. Arakawa, G. Haase, and C. Lifshitz, *J. Phys. Chem.*, 1985, **89**, 2253, and references cited therein.
- 7 H. M. Rosenstock, R. Stockbauer, and A. C. Parr, *J. Chem. Phys.*, 1980, **73**, 773.
- 8 W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness, and J. L. Wood, *J. Am. Chem. Soc.*, 1973, **95**, 7878; W. E. Billups, W. A. Rodin, and M. M. Haley, *Tetrahedron*, 1988, **44**, 1305; W. E. Billups, *Acc. Chem. Res.*, 1978, **11**, 245; B. Halton, *Chem. Rev.*, 1973, **73**, 113.
- 9 Y. Apeloig and D. Arad, *J. Am. Chem. Soc.*, 1986, **108**, 3241.
- 10 F. Brogli, E. Giovannini, E. Heilbronner, and R. Schurter, *Chem. Ber.*, 1973, **106**, 961.

† The measurements were performed using an AEI MS9 mass spectrometer and analysed by applying the Johnstone–McMaster method: R. A. W. Johnstone and B. N. McMaster, *J. Chem. Soc., Chem. Commun.*, 1973, 730. The A.E. reported is the average of 2 independent measurements.

‡ As the measured A.E.(2) represents an upper limit (our experimental set-up does not permit to correct for possible 'kinetic shift' effects. See for example, C. Lifshitz, *Mass Spectrom. Rev.* 1982, **1**, 309), the actual stabilization energy of (2) relative to (1a) may be larger than the measured value.

§ In agreement with this assumption, according to MNDO calculations the difference between the heats of formation of the corresponding chlorides, (5b) and (6b), is 68.5 kcal/mol.