ORGANIC
LETTERS

2010
Vol. 12, No. 21
4880−4883

Aromatization of Fulvene by Complexation with Lithium

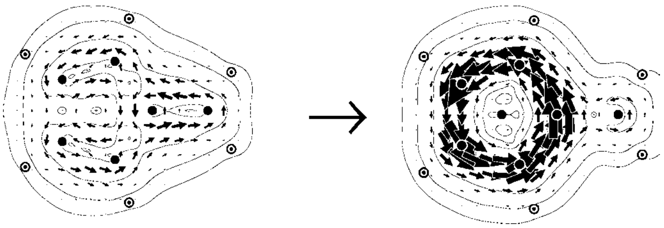
W. P. Oziminski,[*,†] T. M. Krygowski,[‡] P. W. Fowler,[*,§] and A. Soncini[¶]

National Medicines Institute and Institute of Nuclear Chemistry and Technology,
Warsaw, Poland, Department of Chemistry, University of Warsaw,
02 093 Warsaw, Poland, Department of Chemistry, University of Sheffield,
S3 7HF, United Kingdom, and Institute for Nanoscale Physics and Chemistry,
K.U.Leuven, B-3001 Heverlee, Belgium

wojozim@gmail.com; P.W.Fowler@sheffield.ac.uk

Received August 27, 2010

ABSTRACT



At the B3LYP/6-311++G(d,p) level, approach of a lithium atom to a face of the fulvene molecule leads to formation of a complex with binding energy 41 kcal/mol and significant ion-pair character. The fulvene moiety gains a delocalized aromatic cyclic π system, documented by the geometry-based aromaticity index HOMA, and a strong diatropic ring current, visualized by ipsocentric calculation of the π current-density, which leads to an "aromatic" NICS value of -11 ppm.

Fulvene, a nonalternant conjugated hydrocarbon, has a ring that does not follow the magic Hückel $4N + 2$ rule,[1] has low stability,[2,3] low susceptibility exaltation,[4] no π diatropic ring current,[5] significant bond length alternation,[6,7] and high reactivity.[8,9] Increased stability and aromatic character is predicted for fulvene derivatives with electron-donating groups at the C6 *exo* position.[10,11] Aromaticity indices (geometry-based HOMA,[12,13] aromatic stabilization energies,[14] and magnetism-based NICS[15]) are linearly correlated[16] for exo derivatives, and follow the Hammett rule[17] in that the more electron-donating the substituent, the more aromatic the ring.[18] These observations are not surprising, as the $4N + 1$ ring of fulvene has a capacity for six π-electrons and hence a π-withdrawing tendency. Where the ring can gain π-electrons

---

[†] National Medicines Institute & Institute of Nuclear Chemistry and Technology.

[‡] Department of Chemistry, University of Warsaw.

[§] Department of Chemistry, University of Sheffield.

[¶] Institute for Nanoscale Physics and Chemistry, K.U.Leuven.

(1) Streitwieser, A., Jr. *Molecular Orbital Theory for Organic Chemists*; John Wiley: New York, 1961; pp 256ff.

(2) Hess, B. A., Jr.; Schaad, L. J. *J. Org. Chem.* **1972**, *37*, 4179.

(3) Stepien, B. T.; Krygowski, T. M.; Cyranski, M. K. *J. Org. Chem.* **2002**, *67*, 5987.

(4) Dauben, H. J.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1969**, *91*, 1991.

(5) Havenith, R. W. A.; Fowler, P. W.; Steiner, E. *J. Chem. Soc., Perkin. Trans. 2* **2002**, 502.

(6) Wingert, L. M.; Staley, S. W. *Acta Crystallogr.* **1992**, *B48*, 782.

(7) Krygowski, T. M.; Ciesielski, A.; Cyranski, M. K. *Chem. Pap.* **1995**, *49*, 128.

(8) Lloyd, D. *The Chemistry of Conjugated Cyclic Compounds: to be or not to be like benzene*; John Wiley & Sons: Chichester, UK, 1990; pp 91ff.

(9) Kedziorek, M.; Mayer, P.; Mayr, H. *Eur. J. Org. Chem.* **2009**, *8*, 1202.

(10) Ammon, H. L. *Acta Crystallogr.* 1974, *B 30*, 1731.

(11) Peterson, M. L.; Strand, J. F.; Markotan, T. P.; Morales, C. A.; Scaltrito, D. V.; Staley, S. W. *J. Org. Chem.* **1999**, *64*, 9067.

(12) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, 3839.

(13) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70.

(14) Cyrañski, M. K. *Chem. Rev.* **2005**, *105*, 3773.

(15) Schleyer, P. v. R.; Maerker, C.; Dransfeld, H.; Jiao, H.; van Eikemma Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(16) Stêpieñ, B. T.; Krygowski, T. M.; Cyranski, M. K. *J. Org. Chem.* **2002**, *67*, 5987.

(17) Hammett, L. P. *Physical Organic Chemistry*; McGraw-Hill: New York, 1940.

10.1021/ol102037e

and increase delocalization, this tendency is expected to lead to an increase of aromaticity. The object of the present paper is to study how this aromatization process might be realized in an intermolecular context. The model system is the complex formed by approach of a single lithium atom to the ring of fulvene, and the aim is to investigate how the position of the Li center affects the electronic and geometric properties of the ring moiety.

Calculations used Gaussian 03[19] interfaced with NBO 5.G.[20] A B3LYP/6-31G(d,p) reaction-coordinate study used constrained optimization with the distance between ring-center and C1 held at 1.230 Å, and the distance from Li to ring center varied stepwise. For each point, Natural Bond Order analysis and aromaticity indices were calculated: geometry-based HOMA,[12,13] π-electron population based pEDA[21] index (used to analyze aromaticity in fulvene derivatives),[22,23] and magnetism-based NICS(0).[14] pEDA(F) for fulvene is[22] the sum of occupations of $2p_z$ Natural Atomic Orbitals (NAO) over ring carbon atoms, with subtraction of the initial nominal unit populations; it measures π-electron excess in the fulvene ring, and can be taken as an indicator of aromaticity: if 0, the fulvene is nonaromatic; if 1, the fulvene has a full π-sextet and is presumed fully aromatic. Natural Energy Decomposition Analysis (NEDA) was performed with GAMESS(US)[24] interfaced with the NBO 5.G program. The equilibrium structure of the Li−fulvene complex was established by B3LYP/6-311++G(d,p) optimization, checked by diagonalization of the Hessian.

For a check on (magnetic) aromaticity of the system, a current-density map was calculated, to establish the existence of a π-ring current. All-electron and π-only current densities were calculated in the planes at $1a_0$ from the ring faces, using restricted open-shell Hartree−Fock (ROHF) theory with the ipsocentric[25] choice of origin. This choice has advantages of accuracy, efficiency, and interpretability, and gives a direct visual answer to the question of aromaticity in terms of a map that shows existence, sense, and strength of ring current. Current-density calculations used the open-shell version[26,27] of the SYSMO software[28] with the 6-31G(d,p) basis set.

Table S1 (Supporting Information) gives computed data that describe how electronic and geometric properties change with distance between Li and the ring, *d*(Li−fulv), for direct approach of lithium along a line perpendicular to the ring with a fixed right triangle C1−X7−Li where the ring center X7 is 1.230 Å from C1. As Figure 1 shows, these constrained calculations indicate an energy minimum in the region of 1.75 Å with well depth ∼40 kcal/mol.

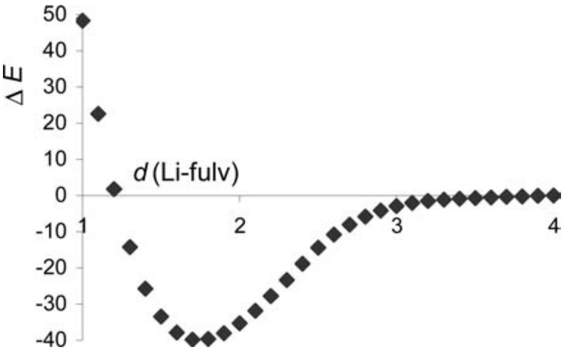


Figure 1. Relative energy, Δ*E* (kcal/mol), of the Li−fulvene complex relative to neutral fragments, as a function of the distance from Li to the ring center, *d*(Li−fulv) (Å).

Full optimization confirms the existence of a local minimum with C_s symmetry (Figure 2). The projection of Li onto the fulvene ring is almost equidistant from all five carbon centers, and the geometry of the ring is essentially planar, no dihedral angle exceeding 1°.

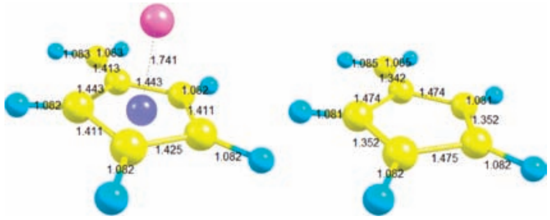


Figure 2. Computed structures of the Li−fulvene complex and the free fulvene molecule (B3LYP/6-311++G(d,p) level).

With inclusion of (small) zero-point energy (ZPE) and Basis-Set Superposition Error (BSSE) corrections, the predicted energy gain on formation of the complex from neutrals is 41.3 kcal/mol. In detail, uncorrected energies of complex and neutral

---

(18) Stêpieñ, B. T.; Cyrañski, M. K.; Krygowski, T. M. *Chem. Phys. Lett.* **2001**, *350*, 537.

(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision E.01; Gaussian, Inc., Wallingford, CT, 2004.

(20) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(21) Oziminñski, W. P.; Dobrowolski, J. C. *J. Phys. Org. Chem.* **2009**, *22*, 769.

(22) Oziminski, W. P.; Krygowski T. M. *J. Mol. Model.* **2010**, in press.

(23) Krygowski, T. M.; Oziminski, W. P.; Palusiak, M.; Fowler, P. W.; McKenzie, A. D. *Phys. Chem. Chem. Phys.* **2010**, *12*, 10740.

(24) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

(25) Steiner, E.; Fowler, P. W. *J. Phys. Chem.* **2001**, *105*, 9553.

(26) Soncini, A. *J. Chem. Theory Comput.* **2007**, *3*, 2243.

(27) Soncini, A.; Fowler, P. W. *Chem. Phys. Lett.* **2008**, *450*, 431.

(28) Lazzeretti, P.; Zanasi, R. *SYSMO package*, University of Modena, 1980; additional routines by Steiner, E., Fowler, P. W., Havenith, R. W. A., and Soncini, A.

fragments are −239.813737, −232.255238, and −7.491333 for fulvene−Li, fulvene and Li, respectively (all in au). The ZPE is +0.097718 for the complex, and +0.097480 for free fulvene. With a BSSE of +0.001083 with respect to neutral fragments, this yields a dissociation energy of +0.065845 au. The analysis for charged fragments gives −232.270565 and −7.284918 for fulvene anion and Li cation, ZPE of +0.092528 for the anion, BSSE of +0.001442, and hence an energy of dissociation to ions of +0.251622 au (158 kcal/mol). The dissociative mode lies at 543 cm^{-1}.

The significant stabilization of the Li−fulvene complex is associated with charge transfer from Li to the fulvene moiety (over 90% of an electron according to the NBO analysis which gives $q(\text{Li}) = +0.912e$ near the minimum (see Table S1, Supporting Information)). This electron transfer is manifested in an increased π population in the fulvene ring, which according to pEDA(F) gains ~80% of an electron, taking it closer to the magic $4N + 2$ Hückel count. The changes in the ring π population are greater than those produced by exocyclic substitution: replacement of the *exo* CH_2 with neutral substituents leads to at most 0.31 (for NMe_2), and even for charged substituents the maximum was 0.70 (for CH_2^-).[23] This implies more efficient through-space transfer of charge from the Li atom on the face of the fulvene π system, compared to though-bond inductive and mesomeric effects of exo substituents. Bond length changes in the fulvene ring are reflected in the increase of the HOMA aromaticity index from ~0 for fulvene[29] to higher values near the equilibrium structure. At the same time, the C1−C6 bond lengthens by ~0.07 Å, suggesting a change from double bond in the isolated molecule to aromatic bond in the complex.

Notably, the various indicators show a sharp change in behavior for $d(\text{Li−fulv}) \approx 2.5$ A (Figure 3a−e), which places the equilibrium structure on a plateau of property values all broadly indicative of aromaticity. In this region, the indicators correlate well with each other, suggesting that they describe a common underlying trend of aromatization of the fulvene as the complex forms. It is tempting to interpret ~2.5 Å as the point at which electron transfer happens, the electronic structure gains significant ion-pair character, and the fulvene moiety becomes aromatic. Evidence in support of the implied charge transfer comes from Natural Energy Decomposition Analysis (Figure 4) for points along the approach pathway.

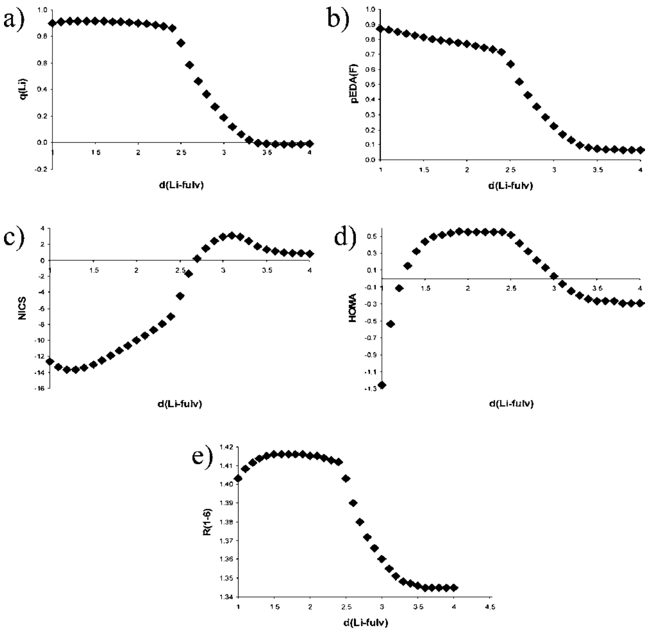


Figure 3. Variation of electronic and geometric indices with approach of Li to the fulvene ring: (a) $q(\text{Li})$, the NPA charge on the Li center (e), (b) pEDA(F) index of ring π population, (c) HOMA, (d) NICS(0), and (e) C1−C6 bond length (Å).

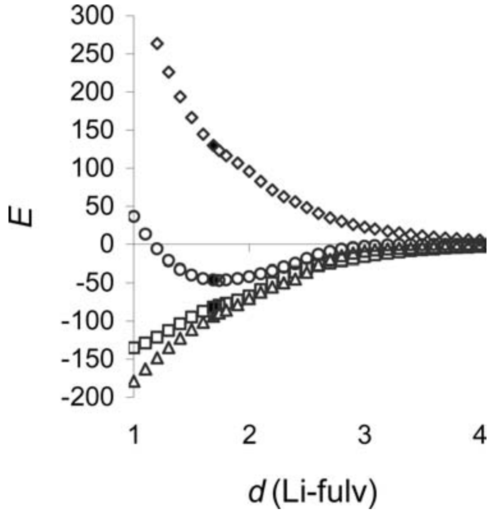


Figure 4. Natural energy decomposition analysis[30,31] (NEDA) for the interaction energy as Li approaches fulvene. Calculations were performed at the B3LYP/6-31G(d,p) level for the curves. Key: EL = electric (squares), CT = charge transfer (triangles), CORE = Pauli repulsion (diamonds), and TOTAL = total interaction (circles). Energies are in kcal/mol and distances in Å. Filled symbols represent the equilibrium structure.

The summed energy reproduces the bound-state curve observed in Figure 1, and the Pauli repulsion term (CORE) shows the expected exponential-type increase as the atomic cores approach. The attractive contributions are the Electric (EL) and Charge-Transfer (CT) terms. EL (electrostatic and polarization) dominates at long range, but the two curves cross at ~2.5 Å, pointing to a switchover to a "charge transfer region". For the equilibrium structure, the B3LYP/6-311++G(d,p) energy decomposition is (in kcal/mol) the following: CT −108, EL −83, CORE 144, and TOTAL −49 (at the B3LYP/6-31G(d,p) level the decomposition is similar: CT −90, EL −79, CORE 123, and TOTAL −46 kcal/mol). The difference between NEDA TOTAL and calculated binding energies arises because the NEDA reference is the monomers at its geometry in the complex.

Additional support for the attribution of aromaticity to the Li−fulvene complex at the equilibrium geometry comes from

---

(29) Krygowski, T. M.; Ciesielski, A.; Cyranski, M. K. *Chem. Pap.* **1995**, *49*, 128.

(30) Glendening, E. D. *J. Am. Chem. Soc.* **1996**, *118*, 2473.

(31) Glendening, E. D. *J. Phys. Chem. A* **2005**, *109*, 11936.

calculations based on the magnetic criterion. Some caution is needed in interpreting NICS values[32] and current-density maps[26,27] for open-shell systems and there are well-known experimental difficulties with such systems. The induced current density is first order in the external field, and governs the second-order chemical shifts and magnetic susceptibility. In experiments, these aromaticity-related response properties can be masked by the larger first-order energy arising from the permanent spin magnetic moment and other effects, but, nonetheless, they remain indicators of the underlying electronic structure, just as in closed-shell systems. Here, the single-point NICS(0) value[14] calculated at the B3LYP/6-311++G(d,p) level is 0.94 ppm for fulvene itself, indicating nonaromaticity, but is −11.15 ppm for the complex, which is similar to the value for benzene itself, and in the absence of perturbing effects, is an indication for a typical aromatic ring.

The presence of the diatropic ring current implied by NICS is confirmed by direct calculation of the current-density map (Figure 5), which shows a clear induced diatropic circulation around the five-membered ring. Correlations with free fulvene were used to identify the molecular orbitals of the complex with approximate π character in the lower symmetry of the complex, and their orbital contributions were summed to give the π current, arising in principle from three doubly occupied and one singly occupied canonical molecular orbitals, but in practice, in the ipsocentric ROHF approximation, dominated by the near-degenerate pair of doubly occupied orbitals of highest energy. This dominance of current by frontier π orbitals is exactly as expected for an aromatic ring in the ipsocentric model of diatropic currents in aromatic systems.[33] The current in the map is also of about the same strength as the archetypal benzene π current calculated at the same level of theory: the maximum value of the current in the $1a_0$ plotting plane, parallel to the median plane of the carbon atoms, is 0.087 au on the open face of the complex, and 0.061 au on the attachment face, compared to 0.080 au for the more symmetrical flow in benzene. The fulvene moiety in the complex is therefore predicted to be aromatic on the ring-current criterion.

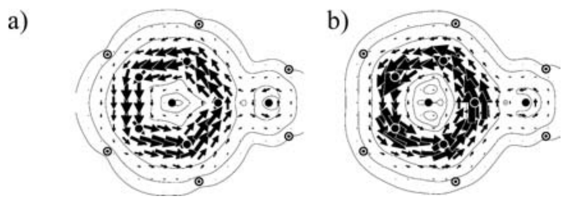


Figure 5. Current density induced in the π electron distribution of the fulvene moiety of the Li••fulvene complex by a perpendicular magnetic field, in planes $1a_0$ (a) above (Li side) and (b) below (open side) the ring. The equilibrium B3LYP/6-311++G(d,p) structure is used, and calculation of currents is in the ipsocentric formulation[25] at the ROHF/6-31G(d,p) level. The map shows summed orbital contributions of one singly and three doubly occupied π-like orbitals. Contours show magnitude and arrows the in-plane projection of induced current density per unit applied field. Diatropic (aromatic) circulation is counterclockwise.

In conclusion, calculations point to the viability of a thermodynamically stable Li••fulvene radical complex with substantial ion-pair character in the gas phase, and with various geometric, electronic, and magnetic indicators attributing aromaticity to the fulvene moiety within that complex. In this sense, fulvene is predicted to be aromatized by the approach of a lithium atom.

Acknowledgment. A.S. thanks INPAC (Institute for Nanoscale Physics and Chemistry) for financial support. Computational Grant G31-10 from the Interdisciplinary Centre of Mathematical and Computer Modelling (ICM) at Warsaw University is gratefully acknowledged.

Supporting Information Available: Tables S1 and S2 give the calculated data for interaction properties plotted in Figures 2−4, and optimized Cartesian coordinates for the complex are given in Table S3. This material is available free of charge via the Internet at http://pubs.acs.org.

OL102037E

---

(32) Gogonea, V.; Schleyer, P. v. R.; Schreiner, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1945.

(33) Steiner, E.; Fowler, P. W. *Chem. Commun.* **2001**, 2220.