provide a critical element of 1,2-stereocontrol via Lewis acid complexation in these cyclizations. A variety of scalemic cyclitols could, in principle, be prepared from pentoses via our stereodivergent vinylsilane–aldehyde cyclization strategy.

Acknowledgment. This work was supported by the National Institutes of Health (CA-34303).

Supplementary Material Available: Experimental and spectral data for all new compounds, ^{13}C NMR spectra for compounds 5, 6, 7, 9, 10, 11, 12, 13, and 14, and ^{1}H NMR spectra for compounds 11 and 12 (15 pages). Ordering information is given on any current masthead page.

Articles

Relationships between the Aqueous Acidities of Some Carbon, Oxygen, and Nitrogen Acids and the Calculated Surface Local Ionization Energies of Their Conjugate Bases

Tore Brinck, Jane S. Murray, and Peter Politzer*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received March 12, 1991

Average local ionization energies ($\bar{I}(\mathbf{r})$) have been computed on the molecular surfaces of the conjugate bases for four different groups of carbon and oxygen acids using an ab initio self-consistent-field molecular orbital approach. The lowest surface $\bar{I}(\mathbf{r})$ ($\bar{I}_{S,\min}$) are generally found on the atom from which the proton has been abstracted. Good linear relationships between aqueous acidities and $\bar{I}_{S,\min}$ are found for the different groups. A single linear relationship between pK_a and $\bar{I}_{S,\min}$ that includes the four groups and three additional nitrogen acids also exists; the correlation coefficient is 0.97. This provides a means for predicting the pK_a's of a large variety of carbon, oxygen, and nitrogen acids.

Introduction

Acidity is a fundamental and very practical chemical concept. Although acidities have long been evaluated experimentally, their determination by computational techniques encounters significant problems.[1,2] Accurate calculation of gas-phase acidities requires the use of ab initio methods with large basis sets that include diffuse functions,[1,2] thus limiting the sizes of the systems that can be treated. The calculation of solution acidities is even more demanding since quantum chemical approaches must be supplemented by statistical mechanical considerations.[2]

We have recently shown, for a series of azines and azoles, that an excellent correlation exists between the lowest values of the average local ionization energies $\bar{I}(\mathbf{r})$, computed on their gas-phase three-dimensional molecular surfaces, and the aqueous solution acidities (pK_a's) of their conjugate acids.[3] In this study, we explore possible extensions of this relationship to other classes of acids. We show that there exist linear relationships between our calculated $\bar{I}(\mathbf{r})$ values and the experimentally determined pK_a's of the conjugate bases of a variety of carbon, nitrogen, and oxygen acids.

Table I. Experimentally Determined pK_a's and Calculated $\bar{I}_{S,\min}$ for Some Substituted Methanes

conjugate base	conjugate acid pK_a[a]	$\bar{I}_{S,\min}$ (eV) [6-31G*/3-21G]
CH_3^-	40.	0.101
CH_2CN^-	25.	2.906
$CH(CN)_2^-$	11.2	5.475
$CH_2NO_2^-$	10.2	5.630
$CHClNO_2^-$	7.2[b]	7.179
$CH(NO_2)_2^-$	3.6	7.622
$C(NO_2)_3^-$	0.1	8.917
$C(CN)_3^-$	−5.0[c]	7.712
$C(NO_2)_2CN^-$	−6.2	9.052

[a] Reference 12. [b] Reference 13. [c] Measured in aqueous sulphuric acid.[12]

$\bar{I}(\mathbf{r})$ has recently been introduced as a useful property for studying molecular reactivity.[3-5] It is rigorously defined within the self-consistent-field molecular orbital (SCF-MO) framework by eq 1. $\rho_i(\mathbf{r})$ is the electronic

$$\bar{I}(\mathbf{r}) = -\sum_i \frac{\rho_i(\mathbf{r})\epsilon_i}{\rho(\mathbf{r})} \qquad (1)$$

density at the point $\mathbf{r}$ of the ith molecular orbital, having an orbital energy ϵ_i, and $\rho(\mathbf{r})$ is the total electronic density. According to Koopmans' theorem, the energy required to remove an electron can be approximated by the absolute value of its orbital energy.[6] $\bar{I}(\mathbf{r})$ can therefore be interpreted as the average energy required to remove an electron from any point $\mathbf{r}$ in the space of an atom or molecule. At those points where $\bar{I}(\mathbf{r})$ has its lowest values are to be

---

* Author to whom correspondence should be addressed.

[1] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, P. *Ab Initio Molecular Orbital Theory*; Wiley and Sons: New York, 1986.

[2] Jorgensen, W. L.; Briggs, J. M. *J. Am. Chem. Soc.* 1990, *111*, 4190.

[3] Brinck, T.; Murray, J. S.; Politzer, P.; Carter, R. E. *J. Org. Chem.* 1991, *56*, 2934.

[4] Sjoberg, P.; Murray, J. S.; Brinck, T.; Politzer, P. *Can. J. Chem.* 1990, *68*, 1440.

[5] Murray, J. S.; Seminario, J. M.; Politzer, P.; Sjoberg, P. *Int. J. Quantum Chem.*, Quantum Chem. Symp. 1990, *24*, 645.

[6] Koopmans, T. A. *Physica* 1933, *1*, 104.

0022-3263/91/1956-5012$02.50/0

Table II. Experimentally Determined pK_a's, Gas-Phase Protonation Enthalpies, and Calculated $\bar{I}_{S,min}$

conjugate base	conjugate acid pK_a	protonation enthalpy[c] (kcal/mol)	$\bar{I}_{S,min}$ (eV) [6-31G*/3-21G]	$\bar{I}_{S,min}$ (eV) 6-31+G*/6-31G*]
CH_3^-	40[a]	−416.6	0.101	1.248
$H_2C{=}CH^-$	36.5[a]	−406.0	1.700	2.376
$HC{\equiv}C^-$	25[a]	−375.4	3.61 (3.552)[d]	4.408[d]
CH_2CN^-	25[b]	−372.1	2.906	4.549
$CH_2NO_2^-$	10.2[b]	−358.7	5.630	4.832
CN^-	9.2[b]	−353.1	4.957	5.756

[a] Reference 1. [b] Reference 12. [c] Reference 14. [d] This $I_{S,min}$ is found between the carbons, closer to the one bearing the hydrogen.

Table III. Some Experimentally Determined Properties and Calculated $\bar{I}_{S,min}$ for a Series of Carboxylic Acids

conjugate base	conjugate acid pK_a[a]	ΔH of protonation[b] (kcal/mol)	ΔG of protonation[b] (kcal/mol)	$\bar{I}_{S,min}$ (eV) [6-31G*/3-21G]
CH_3COO^-	4.76	−348.5	−341.5	7.264
$HCOO^-$	3.75	−345.2	−338.2	7.250
CH_2ClCOO^-	2.86	−335.4	−328.8	8.197
CH_2FCOO^-	2.66	−337.6	−331.0	7.696
$CHCl_2COO^-$	1.30	−328.4	−321.9	8.813
$HOOCCOO^-$	1.19			9.041

[a] The pK_a values are taken from ref 17, except for that of CH_2FCOO^-, which is taken from ref 18. [b] Enthalpies and Gibbs free energies of protonation of the carboxylate anions at 300 K in the gaseous phase. Data are taken from ref 19.

Table IV. Experimentally Determined pK_a's and Calculated $\bar{I}_{S,min}$ for a Series of Oxo Acids

conjugate base	conjugate acid pK_a	$\bar{I}_{S,min}$ (eV) [6-31G*/3-21G]
HOO^-	11.65[a]	5.014
OCl^-	7.2[b]	6.399
$HCOO^-$	3.75[c]	7.250
ONO^-	3.40[c]	7.626
$OClO^-$	2.0[b]	8.139

[a] Reference 20. [b] Reference 21. [c] Reference 17.

found the most energetic and easily removed electrons; these should accordingly be reactive sites toward electrophilic attack. We have indeed shown that $\bar{I}(\mathbf{r})$ calculated on molecular surfaces provides site-specific quantitative predictions of reactivity toward electrophiles within different kinds of aromatic systems.[3,4,7] These findings have led us to investigate whether $\bar{I}(\mathbf{r})$ might be related to pK_a,[3] since the latter reflects tendencies to interact with the electrophile H^+ in aqueous solution.

Methods and Procedure

We have used an ab initio SCF-MO approach (GAUSSIAN 88[8]) to calculate optimized structures at the 3-21G level for the anions listed in Tables I–V. For OCl^- and $OClO^-$, the basis set was augmented by a set of polarization functions on the chlorine atoms (3-21G*).[1] The 3-21G and 3-21G* basis sets have been found to provide generally good geometries.[1] Using these structures, average local ionization energies were calculated at the 6-31G* level on molecular surfaces defined by the contour of electron density equal to 0.002 electrons/bohr^3.[9] This contour has been shown to encompass at least 95% of the electronic density and to provide physically meaningful molecular dimensions.[10,11] We have found that the magnitudes of $\bar{I}(\mathbf{r})$ on the surface do not change significantly (less than 1% decrease) in going from the 0.002 to the 0.001 electron/bohr^3 contour. (Since it is believed that diffuse functions are needed to properly describe the electronic structures of anions,[1,2] a preliminary study using the 6-31+G basis set was carried out for the molecules in Table I. We found that in most instances the 6-31G* calculations gave lower total energies and provided better correlations between $\bar{I}(\mathbf{r})$ and pK_a.) For one group of carbanions, $\bar{I}(\mathbf{r})$ was also computed at the 6-31+G* level using 6-31G* optimized geometries.

Table V. Experimentally Determined pK_a's and Calculated $\bar{I}_{S,min}$ for a Series of Nitrogen Acids

conjugate base	conjugate acid pK_a	$\bar{I}_{S,min}$ (eV) [6-31G*/3-21G]
NH_2^-	38.0[a]	1.325
NH_2NH^-	(30.5)[b]	2.313
NH_2CONH^-	17.5[a]	5.143
$NH(NO_2)^-$	6.55[c]	7.075
$N(NO_2)_2^-$	(−5.6)[b]	9.132

[a] Reference 22. [b] This pK_a value is predicted from our general correlation presented in Figure 4. [c] Reference 23.

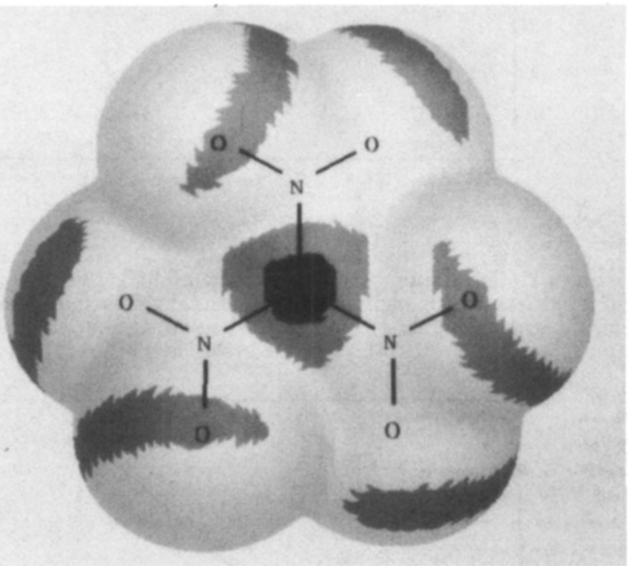


Figure 1. Calculated $\bar{I}(\mathbf{r})$ on the molecular surface of the trinitromethyl anion, $C(NO_2)_3^-$. Three ranges of $\bar{I}(\mathbf{r})$ are depicted, in eV. Black is for $\bar{I}(\mathbf{r}) < 9.5$; gray is for $9.5 < \bar{I}(\mathbf{r}) < 12.3$; white is for $\boldsymbol{I}(\mathbf{r}) > 12.3$.

Results and Discussion

Figure 1 shows $\bar{I}(\mathbf{r})$ on the molecular surface of the trinitromethyl anion, $C(NO_2)_3^-$. The region of lowest $\bar{I}(\mathbf{r})$ is near the carbon, where electrophilic attack is indeed anticipated to be most probable. Local minima are also seen on the oxygens but are larger in magnitude. The lowest surface $\bar{I}(\mathbf{r})$ values for five groups of anions, designated as $\bar{I}_{S,min}$, are listed in Tables I–V. In most cases, $\bar{I}_{S,min}$ is in the vicinity of the atom from which the proton was abstracted to form the anion, as is illustrated for the trinitromethyl anion in Figure 1. The only exceptions to this pattern are the acetylene and the nitrite anions; these will be discussed later.

In Table I are listed the $\bar{I}_{S,min}$ values for nine methyl carbanions, together with the experimentally determined pK_a's of their conjugate acids.[12,13] As is shown in Figure

---

(7) Lane, P.; Murray, J. M.; Politzer, P. *THEOCHEM*, in press.

(8) GAUSSIAN 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol S.; Pople, J. A. GAUSSIAN 88; Gaussian Inc.: Pittsburgh, PA, 1988.

(9) The original programs for computing and plotting properties on molecular surfaces were written by Dr. Per Sjoberg and Mr. Tore Brinck.

(10) Bader, R. F. W.; Preston, H. J. T. *Theor. Chim. Acta* **1970**, *17*, 384.

(11) Bader, R. F. W.; Henneker, W. H.; Cade, P. E. *J. Chem. Phys.* **1967**, *46*, 3341.

(12) Jones, J. R. *The Ionization of Carbon Acids*; Academic Press, London, 1973.

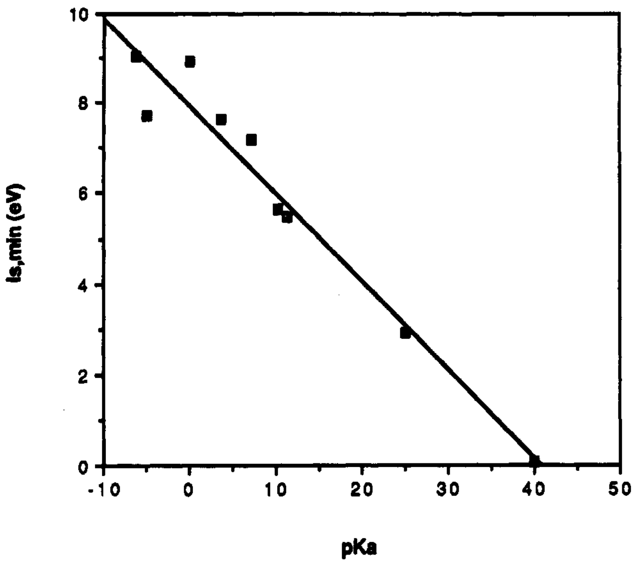


Figure 2. Correlation between calculated 6-31G*/3-21G $\bar{I}_{S,\min}$ of nine methyl carbanions and experimentally-determined conjugate acid pK_a's (Table I). The least-squares equation of the line is $y = 7.9233 - 0.9141x$, with a correlation coefficient of 0.98.

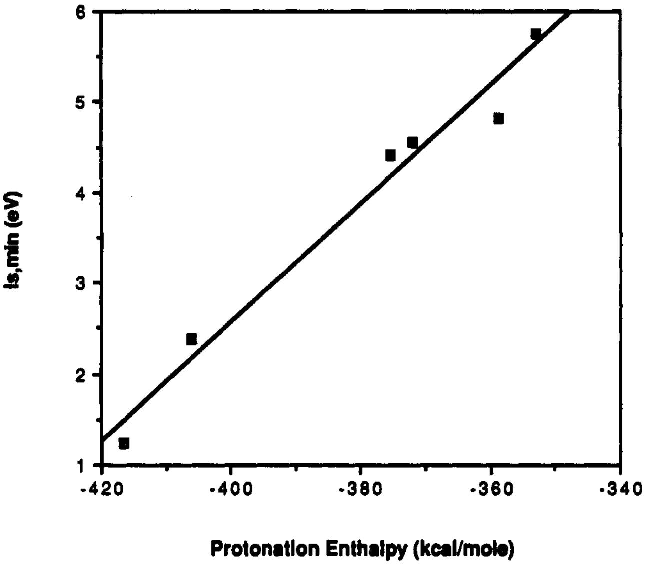


Figure 3. Correlation between calculated 6-31+G*/6-31G* $\bar{I}_{S,\min}$ and experimentally determined protonation enthalpies of six carbanions (Table II). The least-squares equation of the line is $y = 28.6897 + 0.0653x$, with a correlation coefficient of 0.99.

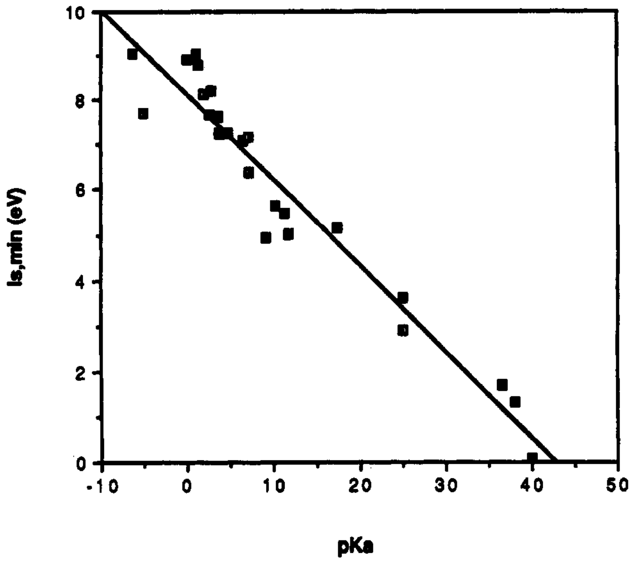


Figure 4. Correlation between calculated 6-31G*/3-21G $\bar{I}_{S,\min}$ of the 25 conjugate bases listed in Tables I–V and experimentally determined conjugate acid pK_a's. The least-squares equation of the line is $y = 8.1307 - 0.1904x$, with a correlation coefficient of 0.97.

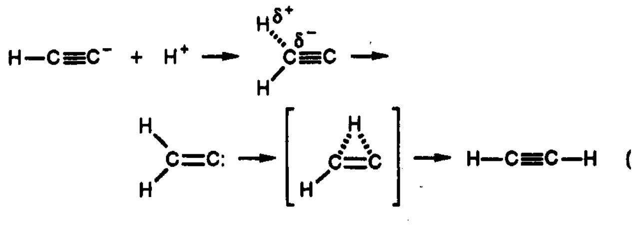
2, a good linear relationship exists between $\bar{I}_{S,\min}$ and pK_a, with a correlation coefficient of 0.98.

Table II gives the $\bar{I}_{S,\min}$, observed gas-phase protonation enthalpies,[14] and pK_a's[1,12] for another, more diverse series of carbanions. There are linear relationships between $\bar{I}_{S,\min}$ (6-31G*/3-21G) and both protonation enthalpies and pK_a's for this group; the correlation coefficients are 0.95 and 0.97, respectively. The former improves to 0.99 when $\bar{I}(\mathbf{r})$ is calculated at the 6-31+G*/6-31G* level (Figure 3); however, the correlation coefficient for pK_a is reduced to 0.93. (It should be noted that there is considerable uncertainty in some of the pK_a values.[2,12])

As mentioned earlier, the $\bar{I}_{S,\min}$ on the molecular surface of the acetylene anion is not found near the ionic carbon. It is located between the carbons and is closer to the one bearing the hydrogen. (This conclusion was confirmed by the 6-31+G*/6-31G* calculation.) These results suggest that the mechanism for protonation might be other than simply what is shown below in eq 2 (and which is what

$$\mathrm{H{-}C{\equiv}C^- + H^+ \rightarrow [H{-}C{\equiv}\overset{\delta-}{C}{\cdots}\overset{\delta+}{H}] \rightarrow H{-}C{\equiv}C{-}H} \quad (2)$$

would be expected from looking at the structures of acetylene and its anion). There may be some tendency for a mechanism such as is depicted in eq 3:



(3)

Vinylidene ($H_2C{=}C{:}$) has been detected experimentally,[15] and numerous calculations have estimated it to be 40–50 kcal/mol higher in energy than acetylene.[1,16] Furthermore, the interconversion from vinylidene to acetylene has been found theoretically to have a low activation barrier of only 3–4 kcal/mol.[16]

In Table III are $\bar{I}_{S,\min}$, pK_a's,[17,18] and measured gas-phase enthalpies and Gibbs free energies of protonation[19] for the anions of a group of carboxylic acids. The relationship between $\bar{I}_{S,\min}$ and pK_a for these six molecules has a correlation coefficient of 0.93; however, this improves to 1.00 when fluoroacetic acid and formic acid are omitted. On the other hand, the latter two fit in quite well when $\bar{I}_{S,\min}$ is plotted against the gas-phase ΔH and ΔG values; the correlation coefficients are 0.96 and 0.97, respectively. This suggests that the pK_a deviations reflect anomalous solva-

---

(13) Adolph, H. G.; Kamlet, M. J. *J. Am. Chem. Soc.* **1966**, *88*, 4761.

(14) Dewar, J. S.; Dieter, K. M. *J. Am. Chem. Soc.* **1986**, *108*, 8075.

(15) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974.

(16) Gallo, M. M.; Hamilton, T. P.; Schaefer, III, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 8714.

(17) Lange, N. A. *Handbook of Chemistry*; Handbook Publishers: New York, 1956.

(18) March, J. *Advanced Organic Chemistry, Reactions Mechanisms and Structure*, 3rd ed.; McGraw Hill: New York, 1985.

(19) Cummings, J. B.; Kebarlé, P. *Can. J. Chem.* **1978**, *56*, 1.

tion effects involving these two molecules.

Table IV lists $\bar{I}_{S,\min}$ and pK_a's[17,20,21] for a group of oxygen acids. As mentioned earlier, the lowest value of $\bar{I}(\mathbf{r})$ on the molecular surface of the nitrite ion is found near the nitrogen, even though the proton was lost by an oxygen. However the difference between the oxygen and nitrogen $\bar{I}_{S,\min}$ values is only 0.02 eV. There is an excellent linear relationship between $\bar{I}_{S,\min}$ and pK_a, with a correlation coefficient of 0.99. This is noteworthy in that the group contains a rather diverse set of molecules and considerable differences in solvent effects might be anticipated.

While the discussion so far has treated different families of acids separately, it is gratifying that all of the 25 included in Tables I–V do satisfy a single $\bar{I}_{S,\min}$ vs pK_a relationship, with a correlation coefficient of 0.97 (Figure 4). This general correlation includes the nitrogen acids NH_3, NH_2CONH_2, and NH_2NO_2, the pK_a's of which are listed in Table V. The relationship shown in Figure 4 provides a capability for predicting the pK_a's of a wide range of molecules (carbon, oxygen, and nitrogen acids). For example, we predict the pK_a of $HN(NO_2)_2$ to be −5.6, comparable to that of the very strong acid $CH(NO_2)_2CN$.

Summary

Good linear correlations have been found between the aqueous acidities of four groups of carbon and oxygen acids and the $\bar{I}_{S,\min}$ values of their conjugate bases. A single linear relationship between pK_a and $\bar{I}_{S,\min}$ that includes all of the systems studied also exists; the correlation coefficient is 0.97. This provides a means for predicting the pK_a's of a large variety of carbon, oxygen, and nitrogen acids.

Acknowledgment. We appreciate the support of this work by the U.S. Army Research Office.

---

[20] Williard, H. L.; Merrit, L. L.; Dean, A. D.; Settle, A. S. *Instrumental Methods of Analysis*, 6th ed.; Litton Educational Publishing: Belmont, CA, 1981.

[21] Ricci, J. E. *J. Am. Chem. Soc.* **1948**, *70*, 109.

[22] Huheey, J. E. *Inorganic Chemistry*, 2nd Ed.; Harper and Row, New York, 1978.

[23] Arrowsmith, C. H.; Awwal, A.; Ester, B. A.; Kresge, A. J.; Lau, P. P. T.; Onwood, D. P.; Tang, Y. C.; Young, E. C. *J. Am. Chem. Soc.* **1991**, *113*, 172.

Photochemistry of 4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene[†]

Christopher Owen Bender,* Douglas Dolman, and Noah Tu

Department of Chemistry, University of Lethbridge, Lethbridge, Alberta, T1K 3M4 Canada

Received January 31, 1991

4-Cyano-2,3-benzobicyclo[4.2.0]octa-2,4,7-triene (**11**) was found to be thermally and photochemically reactive. Heating solutions of **11** at 150 °C for 2 h gave 5-cyanobenzocyclooctatetraene (**10**) quantitatively. The direct irradiation of triene **11** gave 2-cyanobenzosemibullvalene (i.e., SB **12**, 63%, $\Phi = 0.067$), COT **10** (28%, $\Phi = 0.031$), and 1-cyanonaphthalene (ca. 0.5%, $\Phi = 0.0005$). Upon sensitization with *p*-(dimethylamino)benzophenone, **11** gave **12** (30%, $\Phi = 0.028$), COT **10** (9%, $\Phi = 0.0093$), and 1-cyanonaphthalene (2%, $\Phi = 0.0018$). Studies with deuterium-labeled triene (**11a**) revealed that the semibullavene produced from direct irradiation possessed a different label distribution to that obtained from sensitized irradiation, and hence state-dependent pathways operate in the SB formation. The mechanism proposed for the SB formation from S_1 of **11** involves a 1,2-shift with cleavage of the cyclobutene C_1–C_6 bond of the triene, while SB formation from T_1 results from a Zimmerman di-π-methane rearrangement.

Introduction

Semibullvalene derivatives have been shown to be useful starting materials in the synthesis of cyclopentanoid natural products.[1] Recently, we[2-6] and others[7] have reported on the photochemical formation of semibullvalenes (i.e., SB's) from several 2,3-benzobicyclo[4.2.0]octa-2,4,7-trienes (e.g., **1** and **6**). One of our interests in the topic was to determine the effect of varying the site of cyano substitution throughout the aliphatic framework of the triene. To date we have reported on five of the six possible monocyano derivatives, and in all cases SB's have been identified as primary products of the sensitized and/or direct irradiations of the trienes (e.g., **1** → **4**[2]).

Interestingly, the SB's are not produced by a single mechanistic pathway. The results of deuterium-labeling experiments indicate that at least three routes can operate in their formation, the most common of which is a Zimmerman di-π-methane (i.e., DPM) rearrangement[8] involving the two vinyl portions of the triene system (e.g., **1** → **4**, route i, Scheme I[2]). The mechanisms proposed for the less observed pathways involve either a 1,2-shift, with initial cleavage of the cyclobutene C_1–C_6 bond (e.g., **1** → **4**, route ii, Scheme I), or initial bridging between the distal carbons (C-4 and C-8) of the vinyl groups (e.g., **6** → **9**, route iii, Scheme I[3]). We now report on the photochemistry of the remaining cyano derivative **11** and provide evidence for a dramatic excited-state multiplicity dependency on

---

[†] Dedicated to Howard E. Zimmerman on the occasion of his 65th birthday.

[1] (a) Demuth, M. *Mod. Synth. Methods* **1986**, *4*, 89; (b) *Pure Appl. Chem.* **1986**, *58*, 1233. (c) Demuth, M.; Schaffner, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 820. (d) Schaffner, K.; Demuth, M. *Synth. Methods* **1986**, *4*, 61.

[2] Bender, C. O.; Clyne, D. S.; Dolman, D. *Can. J. Chem.* **1991**, *69*, 70.

[3] Bender, C. O.; Dolman, D. *Can. J. Chem.* **1989**, *67*, 82.

[4] Bender, C. O.; Dolman, D.; Murphy, G. K. *Can. J. Chem.* **1988**, *66*, 1556.

[5] Bender, C. O.; Bengtson, D. L.; Dolman, D.; O'Shea, S. F. *Can. J. Chem.* **1986**, *64*, 237.

[6] Bender, C. O.; Cassis, I. M.; Dolman, D.; Heerze, L. D.; Schultz, F. L. *Can. J. Chem.* **1984**, *62*, 2769.

[7] Scheffer, J. R.; Yap, M. *J. Org. Chem.* **1989**, *54*, 2561.

[8] For reviews of the di-π-methane rearrangement, see: (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Essay 16, pp 131–166; (b) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531.