in Table II. In the first set, substituent π donation increases, and electronegativity decreases, from top to bottom. Only the π donor hypothesis can explain the increasing stability of the singlet relative to the triplet in this series. In the second series, substituent electronegativity decreases to a large extent, from top to bottom, while π donation is expected to be small and constant in the whole series. The near constancy of the ST gap in series 2 attests to the insignificance of electronegativity as an influence on the carbene ST gap.

Since $\sum \Delta q_\pi$ has been shown to correlate satisfactorily with the empirical resonance substituent constant, $\sigma_R{}^\circ$,[12] it is not surprising that the calculated ST gaps correlate with $\sigma_R{}^\circ$'s as well. For the Schaefer–Bauschlicher series of halocarbenes in which ST gaps were calculated with double-ζ basis sets plus polarization functions[4,20] (CH_2, CHX, and CX_2, where X = F, Cl, or Br); $E(S) - E(T) = 79.5\sum\sigma_R{}^\circ + 17.0$ ($r = 0.962$). For our STO-3G calculations on 22 carbenes, a remarkably good correlation is obtained as shown in Figure 3: $E(S) - E(T) = 84.5\sum\sigma_R{}^\circ + 43.9$ ($r = 0.969$).

If we assume that the STO-3G ST gaps used in this correlation are consistently overestimated by about 31 kcal/mol, this last equation can be recast into an astonishingly simple relationship for the prediction of carbene ST gaps: $E(S) - E(T) = 84.5\sum\sigma_R{}^\circ + 13$. The empirical resonance substituent constants, $\sigma_R{}^\circ$, are available for a large number of substituents.[13]

In conclusion, the ST gaps of substituted carbenes are determined by π donation or acceptance by the substituents. The electronegativity of the central atom of isovalent species, AH_2, influences the ST gap of the parent,[6] and provides a "scaffold" from which substituents modulate the singlet–triplet gap by π donor or π acceptor effects.

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Delocalized Dicarbanions and Higher Delocalized Carbanions

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Abstract: Simple routes to four new dianions with high resonance energy per atom (REPA) and improved preparations for several other di- and trianions are given. REPA is calculated for delocalized dicarbanions and higher delocalized carbanions which have been prepared and many which have not. Most low molecular weight anions with a charge of less than 0.5 e per atom have REPA's indicating stabilization and most with 0.5 e or more do not. Simple monocyclic anions are calculated to be stabilized or destabilized relative to the corresponding acyclic anions in accordance with the Hückel rule, except that when the charge per atom is large, all of the cyclic anions are destabilized. For linear acyclic and monocyclic systems, REPA is calculated to be maximum at a charge of about 0.17 e per atom. Cyclopentadienyl anion has the largest REPA, and the 13 next highest REPA's belong to some of its di- and trianion derivatives. The calculated values correlate well with the experimental ease of preparation and stabilities of these anions.

Due largely to their bond-forming reactions with a great variety of electrophiles, carbanions are among the most important intermediates in organic synthesis. We report here the synthesis of several new dianions together with calculations of their resonance energies. Calculated resonance energies of many other recently prepared[2] as well as of yet-to-be-prepared dicarbanions and higher carbanions are also given. These calculations correlate well with earlier and new experimental findings on those whose preparation has been attempted. They should help to indicate which new members of this class are worthwhile synthetic goals.

Theory

We have recently shown that the resonance stabilization of ions and radicals can be computed by using the Hückel method in conjunction with a localized reference structure.[3] One of the major difficulties in obtaining a localized reference for ions and radicals was that they, unlike acyclic molecules (e.g., butadiene), have more than one resonance structure as in the allyl cation.

Table I. Ion and Radical Bond Energy Terms

bond type[a]	designation	bond energy, β
$HC–CH_2*$	E_3*	0.6632
HC–CH*	E_2*	0.5996
$C–CH_2*$	$E_2'*$	0.5950
HC–C*	E_1*	0.5480
C–CH*	$E_1'*$	0.5697
C–C*	E_0*	0.5430
$HC*–CH_2*$	E_3**	0.7967
HC*–CH*	E_2**	0.7330
$C*–CH_2*$	$E_2'**$	0.7067
C*–CH*	E_1**	0.6815
C*–C*	E_0**	0.6570

[a] The asterisks refer to positive or negative charges or in the first six bond energy terms to single electrons. We have treated only monoradicals, and the last five bond energies do not apply to these systems.

This problem was overcome by adopting a reference structure containing long (single) and short (double) bonds patterned after that of Mulliken and Parr.[4] Having defined this reference and obtained the reference energy and the resonance energy of the allylic system, all bond energy terms for computing localized

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[1] (a) University of Arizona. (b) Vanderbilt University.

[2] Bates, R. B. In "Comprehensive Carbanion Chemistry"; Buncel, E., Durst, T., Eds.; Elsevier: New York, 1980; pp 1–53.

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[4] Mulliken, R. S.; Parr, R. G. *J. Chem. Phys.* **1951**, *19*, 1271.

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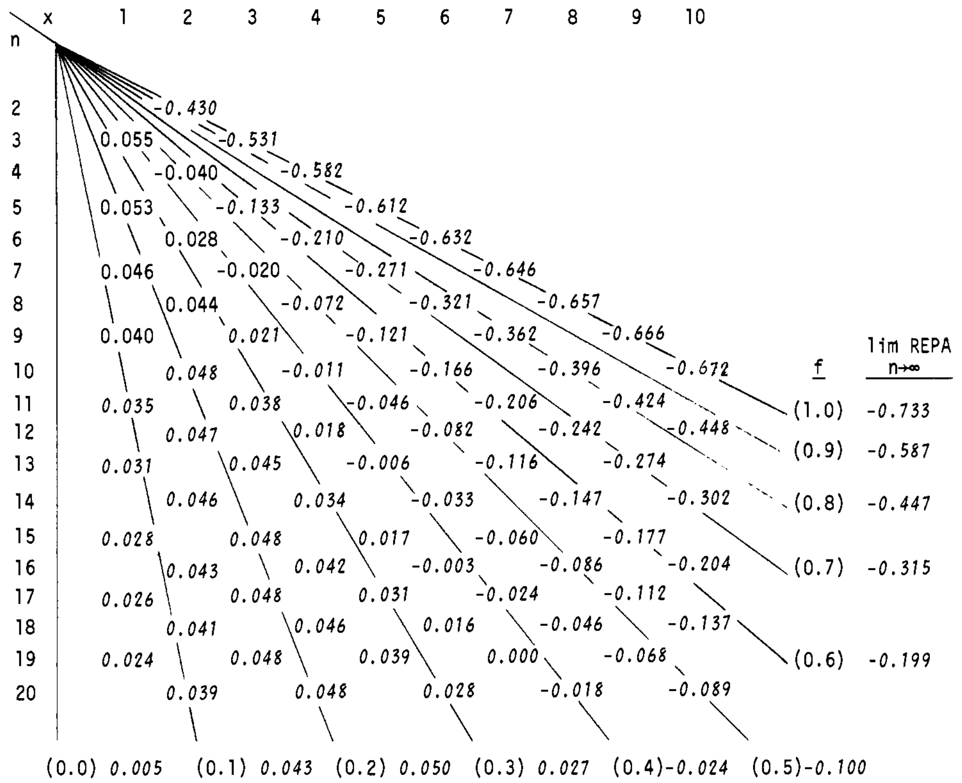


Figure 1. REPA's in units of β for linear carbanions $H-(CH)_n^{-x}-H$ (**1**); anions with italicized REPA's have not been prepared.

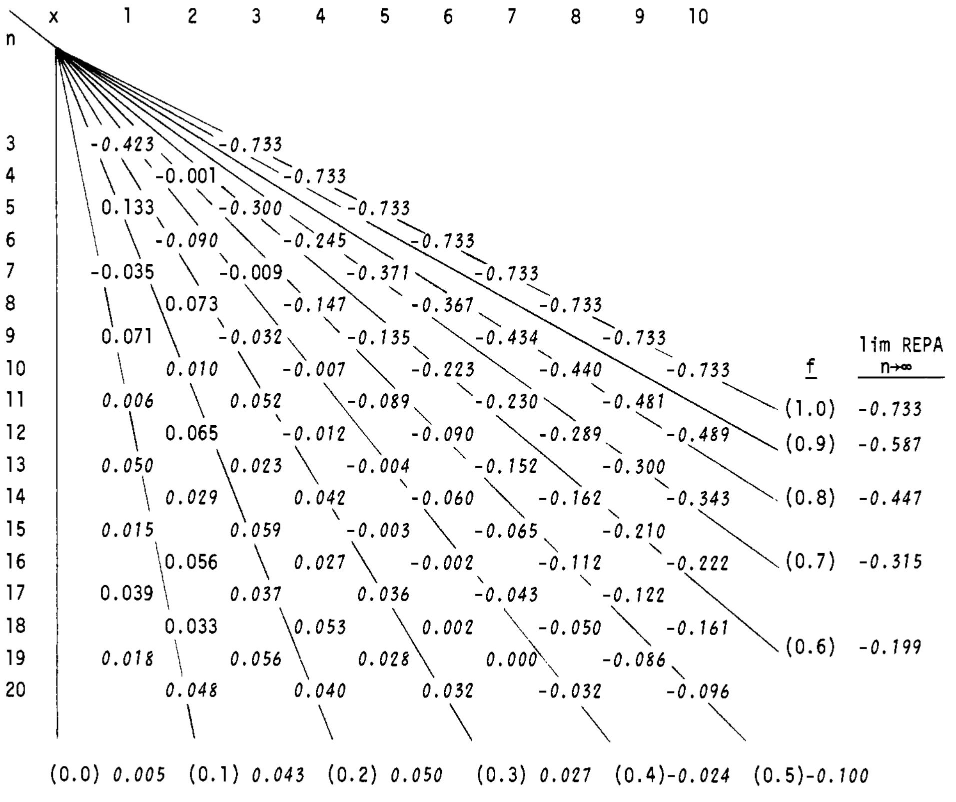


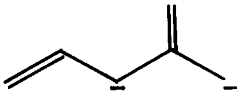
Figure 2. REPA's in units of β for monocyclic carbanions $(CH)_n^{-x}$ (**2**); anions with italicized REPA's have not been prepared.

energies of any conjugated radical or ion were easily gotten and are listed in Table I. Note that the same bond energy terms are used for anions, cations, and radicals.[3]

Anion resonance energies per atom (REPA) are given in Figures 1 and 2 and Tables II and III. All were computed by using

$$\text{REPA} = (1/n)(E_{\pi b} - E_{\text{ref}}) \qquad (1)$$

where n is the number of atoms, $E_{\pi b}$ is the Hückel π binding energy and E_{ref} is the π binding energy of the localized reference structure. For ions and radicals we have chosen to divide the resonance energy by the number of atoms rather than by the number of electrons.[3] Except for the linear and monocyclic anions in Figures 1 and 2, $E_{\pi b}$ was obtained in the usual way by computer diagonalization of the Hückel matrix. Reference energies were calculated by summing appropriate bond-energy terms from Table I and Table I of ref 6 for several resonance structures of an ion and taking an average of these.[5] For example, the localized energy of



is $E_{23} + E_{22'} + E_{2'}^* + E_{1'}^* + E_2^*$. For the linear and monocyclic ions of Figures 1 and 2 it is possible to express REPA in a closed analytical form (see Appendix). Energies and REPA's will be given in units of the Hückel parameter β.

Experimental Section

Nuclear magnetic resonance spectra (NMR) were recorded on a Varian EM-360L or Bruker WM-250 spectrometer in $CDCl_3$; chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a Hitachi Perkin-Elmer Model RMU-6E mass spectrometer. Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Elemental analyses were performed by Industrial Testing Laboratories, Inc., St. Louis, MO. Volatile products were isolated and purified by gas chromatography on a column packed with 10% UCON LB550X on Chromosorb P. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone. Pentane and hexane were washed with sulfuric acid, distilled from $LiAlH_4$, and stored over CaH_2. *n*-Butyllithium in hexane (2.2–2.6 M) was used as received from Alfa Division, Ventron Corp., and potassium *tert*-butoxide was used as received from Aldrich Chemical Co.

Octatetraene Dianion (1, *n* = 8). (*E*)-1,3,7-Octatriene[7] (1.06 g, 10 mmol) in 20 mL of pentane was added dropwise with stirring to 20 mmol of Lochmann's base (2.24 g of potassium *tert*-butoxide and 8.4 mL of 2.4 M *n*-butyllithium in hexane) in 30 mL of pentane under argon. After 30 min, the red precipitate (~70% yield based on quench results) was filtered and washed with pentane. For reactions, it was suspended in 50 mL of dry THF, giving a yellow-green solution. That **1** (*n* = 8) had indeed been prepared was shown by incorporation of 2 deuteriums in a D_2O quench and 2 methyl groups in a methyl iodide quench (MS on the complex mixtures of isomers obtained) and by oxidations with ethylene dibromide[8] to 1,3,5,7-octatetraene,[9] a low-melting solid which polymerized on workup.

Dianion 8. Dropwise addition of 0.8 g (10 mmol) of a mixture of (*E*)- and (*Z*)-3-methyl-1,3-pentadiene to a stirred suspension of 2.5 g (22 mmol) of potassium *tert*-butoxide and 9.3 mL (22 mmol) of 2.4 M *n*-butyllithium in 50 mL of *n*-hexane gave a red precipitate. After refluxing and stirring overnight, the dark red precipitate was filtered and rinsed with pentane. A D_2O quench yielded as the only volatile products a mixture of 60% (*E*)-3-(deuteriomethyl)-5-deuterio-1,3-pentadiene [MS, *m/e* 84; ^1H NMR δ 6.37 (dd, 1 H, J = 17.5, 10.7 Hz), 5.56 (t, 1 H, J = 6.4 Hz), 5.06 (d, 1 H, J = 17.5 Hz), 4.90 (d, 1 H, J = 10.7 Hz), 1.72 (br s, 4 H)] and 40% (*E*)-3-methyl-5-deuterio-1,3-pentadiene [MS, *m/e* 83; ^1H NMR same except 1.72 (br s, 5 H)].

Dianion 14. Dropwise addition of 0.8 g (10 mmol) of 1,3-dimethylenecyclobutane[10] to a stirred suspension of 2.4 g (21.4 mmol) of potassium *tert*-butoxide and 9.1 mL (21.8 mmol) of 2.4 M *n*-butyllithium in 40 mL of pentane under argon gave a bright yellow precipitate. After stirring for 1 h, the precipitate was filtered, rinsed with pentane, and dissolved in 30 mL of THF for further reactions. The yield of dianion **14** was 60% based on the amount of 1-(deuteriomethyl)-4-deuterio-3-methylenecyclobutene [MS, *m/e* 82; ^1H NMR δ 5.6 (br s, 1 H), 4.5 (m, 2 H), other peaks obscured by THF/pentane] obtained on quenching with D_2O.

Fulvene Dianion (16). Adding 0.8 g (10 mmol) of freshly cracked 5-methylcyclopentadiene to 2.5 g (22 mmol) of potassium *tert*-butoxide and 9.3 mL (22 mmol) of 2.4 M *n*-butyllithium in 50 mL of *n*-hexane under argon and stirring and refluxing the resulting suspension for several hours yielded the dipotassium salt of **16** as a burgundy colored precipitate. It was filtered and rinsed with dry pentane several times prior to further reactions (to be discussed elsewhere), which indicated it to have been formed in at least 60% yield.

Trivinylethylene Dianion (32). 3-Vinyl-1,5-hexadiene[7] was metalated analogously to the isomeric octatriene above, yielding the orange dipotassium salt of **32** in 70% yield as indicated by its oxidation to trivinylethylene[11] [^1H NMR δ 5.0–5.3 (m, 4 H), 5.4–5.6 (m, 2 H), 6.0–7.2 (m, 4 H)] by adding a THF slurry dropwise to 1,2-dibromoethane in THF at −78 °C, washing with saturated NaCl, drying over $MgSO_4$, evaporating, and distilling at reduced pressure.

Xylylene Dianions (44–46).[31] On addition of 9.2 mL of 2.4 M *n*-butyllithium (22 mmol) to 2.4 g (21.5 mmol) of potassium *tert*-butoxide, 1.2 mL (10 mmol) of *p*-xylene, and 50 mL of dry olefin-free hexane under argon, a red precipitate formed immediately. The mixture was refluxed for 1 h and cooled to room temperature before filtering and rinsing the dark red anion (**46**, 70% yield) with pentane. The analogous ortho and meta dianions (**44** and **45**, respectively) were prepared from the corresponding xylenes in quantitative yield; the former was red orange and the latter bright yellow.

Characterization of these dianions included quenching with chlorotrimethylsilane. To a stirred suspension of dianion (10 mmol) in 50 mL of pentane, 2.6 mL of chlorotrimethylsilane (20 mmol) was added with stirring. After the anion color had disappeared, the solution was washed with water several times and dried over $MgSO_4$. The solvent was evaporated and the residue distilled (bulb to bulb). Bis(trimethylsilyl)-*p*-xylylene, mp 63–64 °C (lit.[12] 61–63 °C) [^1H NMR δ 0.0 (s, 18 H), 2.0 (s, 4 H), 6.86 (s, 4 H)], was recrystallized from acetone. Bis(trimethylsilyl)-*o*-xylylene [^1H NMR δ 0.55 (s, 18 H), 2.60 (s, 4 H), 7.5 (s, 4 H)] and -*m*-xylylene [^1H NMR δ 0.05 (s, 18 H), 2.1 (s, 4 H), 6.7–7.3 (m, 4 H)], being liquids,[12] were purified by gas chromatography.

Trianion **131**[31] was prepared by adding 1.39 mL (10 mmol) of mesitylene to 5.4 g (48 mmol) of potassium *tert*-butoxide and 20 mL (48 mmol) of 2.4 M *n*-butyllithium suspended in 50 mL of hexane. Upon addition of mesitylene a yellow precipitate formed immediately which darkened to an olive color. The suspension was stirred and refluxed overnight under argon. After cooling to room temperature the anion was filtered and washed with pentane (yield 60%, based on quench products to be described elsewhere). Anions **129** and **130**[31] were prepared analogously in slightly lower yield (~40%).

Results

Calculated REPA's of many dicarbanions and higher carbanions are listed in Figures 1 and 2 and Tables II and III. For radicals and ions, unlike neutral molecules, our method often leads to values of REPA that are significantly different from zero even for acyclic systems. This is in contrast to the graph-theoretical method[13,14] where all acyclics, regardless of charge, are computed to have zero resonance stabilization. The origin of this difference between our results and those of graph theory presumably lies primarily in differences in definition of the reference structure. The evidence to be presented that there are significant differences in the behavior of various open chain ions inclines us toward our reference which does predict these differences.

Figure 1 shows the early members of the linear monoanion series (**1**, x = 1) to be appreciably stabilized; the first four members, allyl (n = 3),[15] pentadienyl (n = 5),[16] heptatrienyl (n = 7),[17] and nonatetraenyl (n = 9)[18] have all been prepared in high concentration. As shown in the Appendix, the limiting REPA as n becomes infinite for any linear series with fixed charge x is the

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(5) Initially we obtained the reference energies of all resonance structures for a large number of systems and took their average. However, it became apparent that this was unnecessary as there was never any significant difference found between the various structures. A similar situation was also found for molecules.[6]

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(7) In our hands, reaction of pentadienylpotassium with allyl chloride (Prevost, C.; Miginiac, P.; Miginiac-Groizeleau, L. *Bull. Soc. Chim. Fr.* **1964**, 2485) gave 3-vinyl-1,5-hexadiene (30%), (*E*)-1,3,7-octatriene (24%), and (*Z*)-1,3,7-octatriene (7%), separable by GC. With GC injector temperatures above 270 °C, these substances Cope rearranged toward an equilibrium mixture of about 90% (*E*)-1,3,7-triene and 10% (*Z*)-1,3,7-triene; at 400 °C, 20% of the 1,5 sigmatropic proton shift product (*E*,*Z*)-1,4,6-octratriene was observed.

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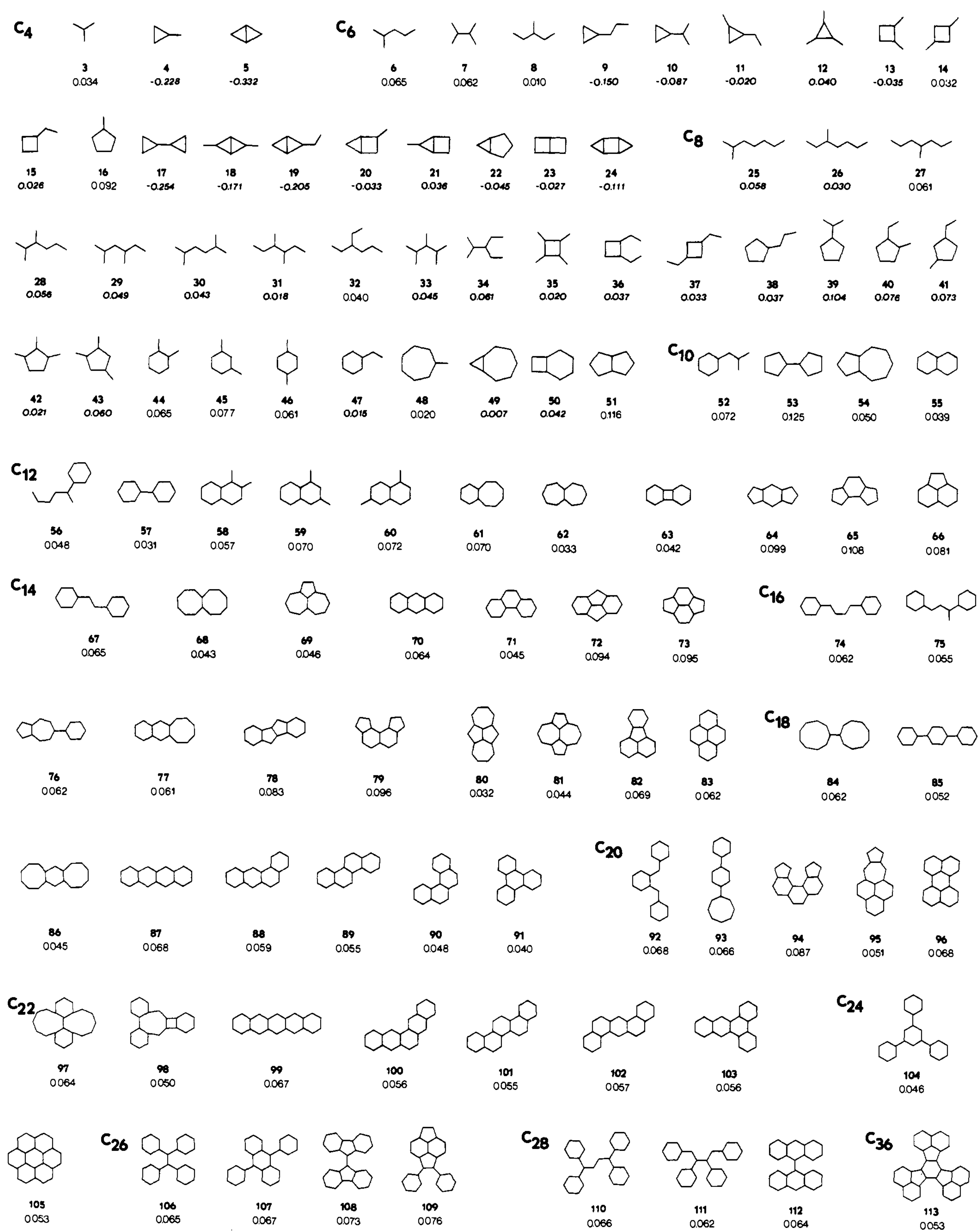
Table II. REPA's of Selected Dicarbanions[a]

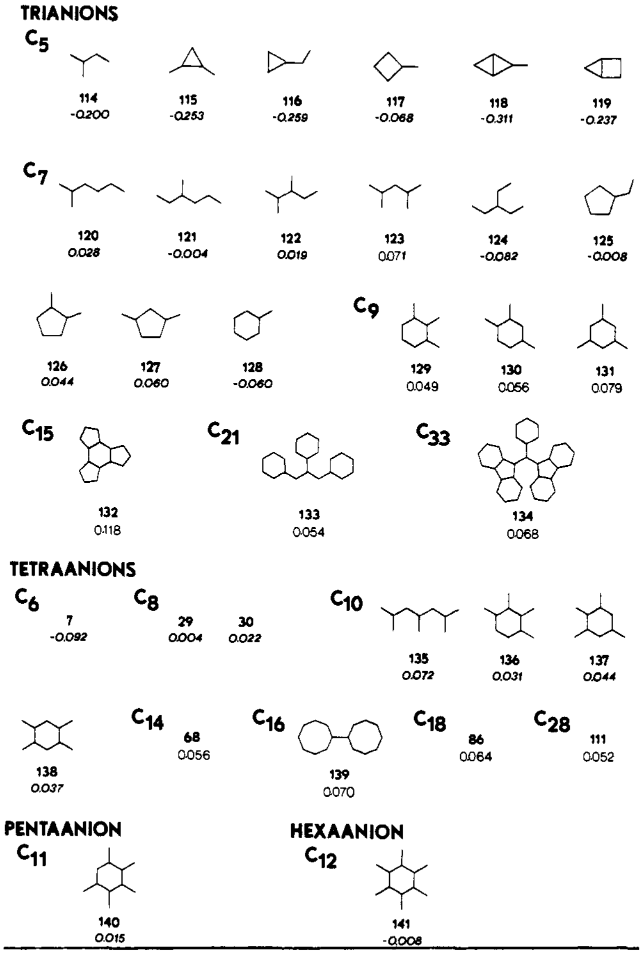


	compd	REPA
C_4	3	0.034
	4	*-0.228*
	5	*-0.332*
C_6	6	0.065
	7	0.062
	8	0.010
	9	*-0.150*
	10	*-0.087*
	11	*-0.020*
	12	*0.040*
	13	*-0.035*
	14	0.032
	15	*0.026*
	16	0.092
	17	*-0.254*
	18	*-0.171*
	19	*-0.205*
	20	*-0.033*
	21	*0.036*
	22	*-0.045*
	23	*-0.027*
	24	*-0.111*
C_8	25	*0.058*
	26	*0.030*
	27	0.061
	28	*0.056*
	29	*0.049*
	30	*0.043*
	31	*0.018*
	32	0.040
	33	*0.045*
	34	*0.061*
	35	*0.020*
	36	*0.037*
	37	*0.033*
	38	*0.037*
	39	*0.104*
	40	*0.076*
	41	*0.073*
	42	*0.021*
	43	*0.060*
	44	0.065
	45	0.077
	46	0.061
	47	*0.015*
	48	0.020
	49	*0.007*
	50	*0.042*
	51	0.116
C_{10}	52	0.072
	53	0.125
	54	0.050
	55	0.039
C_{12}	56	0.048
	57	0.031
	58	0.057
	59	0.070
	60	0.072
	61	0.070
	62	0.033
	63	0.042
	64	0.099
	65	0.108
	66	0.081
C_{14}	67	0.065
	68	0.043
	69	0.046
	70	0.064
	71	0.045
	72	0.094
	73	0.095
C_{16}	74	0.062
	75	0.055
	76	0.062
	77	0.061
	78	0.083
	79	0.096
	80	0.032
	81	0.044
	82	0.069
	83	0.062
C_{18}	84	0.062
	85	0.052
	86	0.045
	87	0.068
	88	0.059
	89	0.055
	90	0.048
	91	0.040
C_{20}	92	0.068
	93	0.066
	94	0.087
	95	0.051
	96	0.068
C_{22}	97	0.064
	98	0.050
	99	0.067
	100	0.056
	101	0.055
	102	0.057
	103	0.056
C_{24}	104	0.046
	105	0.053
C_{26}	106	0.065
	107	0.067
	108	0.073
	109	0.076
C_{28}	110	0.066
	111	0.062
	112	0.064
C_{36}	113	0.053

[a] Anions with italicized REPA's have not been prepared.

"polyacetylene" value of 0.005. On the other hand for series with a fixed ratio $f = x/n$, the limit for infinite n depends on this ratio and has an optimum value of 0.051 at $f = 0.17$. With increasing f the limiting REPA decreases to zero at $f = 0.35$ and then to large negative REPA as f increases further toward 1. Thus, long chains of linearly conjugated double bonds (including polyacetylene) are predicted to be stabilized relative to their reference by the addition of electrons up to about one charge per five atoms.

Table III. REPA's of Selected Tricarbanions and Higher Carbanions[a]



[a] Anions with italicized REPA's have not been prepared.

With the linear dianions and higher anions (**1**, $x > 1$), the first members of the series, where $f > 0.5$, are greatly destabilized by electron repulsion (REPA < -0.1; no molecule with REPA < -0.1 has been prepared). Butadiene dianion (**1**, $x = 2$, $n = 4$),[19,20] hexatriene dianion (**1**, $x = 2$, $n = 6$),[19-21] and octatetraene dianion (**1**, $x = 3$, $n = 7$)[22] are the only members of this series prepared to date. The former has a significantly higher REPA than the further members in the series with $f = 0.5$; this manifestation of increased Coulombic repulsion as negatively charged units are joined can be seen looking down any of the lines joining anions with the same f.

The REPA's in Figure 2 for monocyclic carbanions as expected from the Hückel ($4n + 2$) rule show alternate stabilization (aromaticity) and destabilization (antiaromaticity) compared to the corresponding acylic anions (Figure 1), unless $n \leq 3x - 6$ (above this line, *all* of the cyclic anions are less stable). The observed stabilities of the monoanions **2** ($x = 1$) and dianions ($x = 2$) whose preparation has been attempted fit well with their REPA's as discussed elsewhere.[3] Cycloheptatrienyl trianion (**2**, $x = 3$, $n = 7$) appears to be the only member of this class with more than two negative charges that has been made,[23] though many other cyclic polycarbanions with $f < 0.5$ have REPA's high enough to suggest reasonable stability. The infinite limits for various f's are the same as for the linear polymers, so again the REPA's of large systems are predicted to be increased by the addition of electrons to about one charge per five carbon atoms.

Table II gives REPA's for many further sp^2 hybridized carbon systems with two negative charges. All further four- and six-carbon dianion systems and all acyclic and monocyclic eight-carbon systems except those with three-membered rings are included. Dianions with more than eight carbons which have been reported are also included.

Branched dianion **3**[24] has a much higher REPA than its linearly conjugated isomer (**1**, $x = 2$, $n = 4$), and indeed it is much easier to prepare.[8,19] Two of the branched six-carbon dianions, **6**[19] and **7**,[25] which correspond to two allyl anions joined end to middle and middle to middle, have higher REPA's than the linear isomer (**1**, $x = 2$, $n = 6$) which can be viewed as two allyl anions joined end to end; all three have been made in high concentration. The fourth acyclic isomer (**8**) has the smallest REPA and is formed in very low yield, if at all, under conditions which give the other isomers in good yield;[19] we now report its formation under more vigorous conditions.[22]

The other four- and six-carbon dianions (**4**, **5**, and **9–24**) show widely varying REPA's. We have succeeded in generating two of these anions—**14** from 1,3-dimethylenecyclobutane and **16**, with the highest REPA of any six-carbon dianion, from methylcyclopentadiene[22]—and failed in an attempt to make **13** from 1,2-dimethylenecyclobutane. The latter anion should be quite difficult to make in view of its low REPA; in our attempt, addition to the conjugated diene system occurred rather than metalation, even with Lochmann's base.[25] Derivatives of relatively stable anion **12** have been prepared,[26] but not the parent dianion. The least stable six-carbon dianion is **17**, which consists of two antiaromatic anions (**2**, $n = 3$, $x = 1$) joined by a single bond; though unstable, **17** is stabilized considerably relative to its parent antiaromatic anion (**2**, $n = 3$, $x = 1$), and is the first of four examples in this paper of the generalization that this type of dimer of an antiaromatic ion is stabilized relative to its parent, whereas this type of dimer of an aromatic ion is destabilized compared to its parent.

The differences in the REPA's of the 11 acyclic 8-carbon carbanions **1** ($x = 2$, $n = 8$) and **25–34** can be partly rationalized by noting that the best 4 carbanions (**25**, **27**, **28**, and **34**) are the only ones which can be divided into an allyl anion and a pentadienyl anion *not* joined by charge-bearing atoms, and the worst (**31**) suffers from the same lack of good resonance forms as the worst acyclic 4-carbon (**1**, $x = 2$, $n = 4$) and 6-carbon (**8**) dianions to which it is related. The member with the highest REPA (**27**) has been prepared and it was noted that it was significantly easier to make than **3**, which has a lower REPA.[27] We have now prepared **32**, one of the intermediate REPA members of this series, without difficulty and oxidized it to trivinylethylene.[22]

The cyclic eight-carbon dianions depicted (**35–51** and **2**, $x = 2$, $n = 8$) range from the highly stabilized pentalene dianion (**51**)[28] to the barely stabilized **49**. A particularly striking pair is **38** and **39**, which again illustrate the above-mentioned difference between joining stabilized monoanion systems [in this case allyl = **1** ($x = 1$, $n = 3$) and cyclopentadienyl = **2** ($x = 1$, $n = 5$)] by charge-bearing atoms as in **38** or not as in **39**. Besides the most stable member of this group (**51**), one of the least stable members (**48**)[29] and three of the intermediate stability group (**44–46**)[30-32] have been prepared. Among these last three, the 1,4 isomer (**46**), with the lowest REPA, is clearly the most difficult to prepare by dimetalating the appropriate xylene: with *n*-butyllithium/

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TMEDA, *p*-xylene is dimetalated on the same carbon rather than giving **46**.[31] We have found that *p*-xylene metalates in 70% yield to give **46** with Lochmann's base with no evidence of dimetalation on the same carbon; the greater stability of isomers **44** and **45** is perhaps evidenced by their formation in quantitative yield under the same conditions.[22]

All of the cyclic dianions with 10 or more carbons which have been prepared [**2** (x = 2, n = 12, 16, and 18),[2] **52**,[2] **53**,[33] **54–57**,[2] **58–60**,[34] **61–67**,[2] **68**,[35] **69**,[36] **70–78**,[2] **79**,[37] **80**,**81**,[38] **82–93**,[2] **94**,[37] **95–97**,[2] **98**,[39] **99–113**[2]] have positive REPA's, though there is still considerable variation in calculated stabilization. Compounds **91**, **104**, **113**, and **112** all have ESR spectra indicating diradical ground states; this is expected in the first three cases with their threefold symmetry and is reasonable in the last case due to severe steric interactions in the planar form. Some of the other dianions, notably **2** (x = 2, n = 12) and **97**, are no doubt twisted from coplanarity to some degree by steric interactions or angle strain.

Table III gives REPA's for selected trianions and higher anions, including those reported to have been prepared. All five-carbon trianions [**1** (x = 3, n = 5), **2** (x = 3, n = 5), and **114–119**] have f = 0.6 and appear to be prohibitively destabilized with the exception of methylenecyclobutadiene trianion (**117**); none has been prepared. On the other hand, the seven-carbon trianions selected for inclusion [**1** (x = 3, n = 7), **2** (x = 3, n = 7), and **120–128**], with f = 0.43, have either positive or slightly negative REPA's; the first two and **123**, calculated to be the most stable and divisible into an allyl anion and a 2-methyleneallyl dianion (**3**) joined without serious electrostatic repulsion, have been synthesized.[23] Trianions **129–131**,[31,32] **132**,[40] **133**,[41] and **134**,[42] with nine or more carbons, have all been prepared.

The six-carbon tetraanion (f = 0.67) with the highest REPA is **7**, the only one with a resonance form with four nonadjacent negatively charged carbons and a double bond. Among the best of the eight-carbon tetraanions (f = 0.5) are **29** [butadiene dianion (**1**, x = 2, n = 4) joined favorably to methyleneallyl dianion (**3**)] and **30** (two joined dianions of the latter type). Ten-carbon tetraanion **135** is similarly favored, and the tetramethylbenzene derived tetraanions **136–138** all have promisingly large REPA's though only **137**, with the highest REPA, has been prepared.[31] Other tetraanions which have been reported are cyclooctatetraene dianion "dimer" types **68**,[35] **139**,[43] **86**,[44] and stilbene dianion dimer **111**;[45] all have large REPA's.

Pentaanion **140** and hexaanion **141** appear to be reasonable synthetic goals, even though the latter has f = 0.5.

Comparisons of all the REPA's in this study permit some overall conclusions. Addition of charge to many systems increases REPA to a maximum at $f \sim 0.17$; additional charge decreases REPA rapidly to zero at $f \sim 0.35$ and to very negative values as f increases further. Among acyclics, certain branched members (e.g., dianions **6**, **7**, **27**, and **34** and trianion **123**) have larger REPA's (0.06–0.07) than any of their linear isomers [of which the highest REPA is 0.055 for allyl anion (**1**, n = 3, x = 1)], while other branched isomers (e.g., **8** and **31**) have much lower REPA's (0.01–0.02) than their linear isomers. The highest REPA (0.133) belongs to cyclopentadienyl anion (**2**, n = 5, x = 1), which has $f \sim 0.17$, has only one charge, and is Hückel favored; the next 13 highest REPA's (the *only* others above 0.08) belong to di- and trianions containing at least one cyclopentadienyl anion ring. Slightly less stabilized (REPA's 0.06–0.08) are some other Hückel-favored anions: cyclooctatetraene dianion (**2**, n = 8, x = 2) and its dianion derivatives **61** and **93** and tetraanion derivatives **86** and **139**; benzene derivatives **52**, **59**, **60**, and **131**; and cyclononatetraenyl anion (**2**, n = 9, x = 1) and its derivative **84**.

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Appendix

The Hückel MO coefficients of the linear ions in Figure 1 and the monocycles in Figure 2 all satisfy the finite difference equation

$$\beta c_{i-1} + (\alpha - E)c_i + \beta c_{i+1} = 0 \qquad \text{(A1)}$$

A solution of the form

$$c_i = \sin ia \qquad \text{(A2)}$$

together with the boundary conditions

$$c_0 = c_{n+1} = 0 \qquad \text{(A3)}$$

for the linear systems and

$$c_{n+i} = c_i \qquad \text{(A4)}$$

for the monocycles, where n is the number of carbon atoms, gives the orbital energies

$$\epsilon_j = \alpha + 2\beta \cos [j\pi/(n+1)], \qquad j = 1, 2 ... n \qquad \text{(A5)}$$

for the linear ions and

$$\epsilon_j = \alpha + 2\beta \cos (2\pi j/n), \qquad j = 1, 2 ... n \qquad \text{(A6)}$$

for the monocycles.

None of the systems considered is a radical so that the number of π electrons is even = $2m$. The levels (eq A5) of a linear ion with $2m$ electrons are filled through $j = m$ to give a total π energy of

$$E_\pi = 2m\alpha + 4\beta \sum_{j=1}^{m} \cos \left(\frac{j\pi}{n+1} \right) \qquad \text{(A7)}$$

The sum in eq A7 is the π binding energy $E_{\pi b}$ and can be evaluated by using Lagrange's identity.[46]

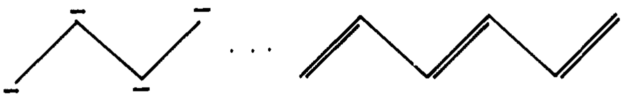
$$E_{\pi b} = 2\beta \left(\sin \left[\frac{(2m+1)\pi}{2(n+1)} \right] \csc \left[\frac{\pi}{2(n+1)} \right] - 1 \right) \qquad \text{(A8)}$$

Expressing this result in terms of the number of atoms n and the negative charge on the ion $x = 2m - n$ gives after some manipulation

$$E_{\pi b} = 2\beta \left(\cos \left[\frac{x\pi}{2(n+1)} \right] \csc \left[\frac{\pi}{2(n+1)} \right] - 1 \right) \qquad \text{(A9)}$$

Since the Hückel method gives only n orbitals, x here and below must not exceed m.

The resonance energy of the linear ions is obtained by subtracting the energy of the reference structure from $E_{\pi b}$. All resonance forms of the reference structure are assumed to be of equal energy[3] and the particular resonance form



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which has one bond each with energy E_{23}, $E_2{}^*$, and $E_3{}^{**}$, $(x - 2)$ bonds with $E_2{}^{**}$, and $(n - x - 2)/2$ each with E_{12} and E_{22} is chosen. Table I and Table I of ref 6 are used to subtract the sum of these bond energies. Then dividing by n gives

$$\text{linear ion REPA } (n,x) = \frac{\beta}{n}\left(2 \cos\left[\frac{x\pi}{2(n+1)}\right] \times \csc\left[\frac{\pi}{2(n+1)}\right] - 1.2680n + 0.5350x - 1.3944\right) \quad \text{(A10)}$$

To avoid radicals, n and x must be of the same parity; eq A10 is valid for both parities.

In the cyclic ions it is necessary to distinguish between even m (i.e., the "4N" systems) and odd m (the "4N + 2" systems); otherwise the treatment is as above and gives

$$\text{even } m \text{ cyclic ion REPA } (n,x) = (\beta/n)(4 \cos [x\pi/(2n)] \times \cot (\pi/n) - 1.2680n + 0.5350x + 0.0002) \quad \text{(A11)}$$

$$\text{odd } m \text{ cyclic ion REPA } (n,x) = (\beta/n)(4 \cos [x\pi/(2n)] \times \csc (\pi/n) - 1.2680n + 0.5350x + 0.0002) \quad \text{(A12)}$$

If eq A10–A12 are written in terms of the ratio $f = x/m$ and the limit taken as m becomes infinite with f fixed, all three cases give

$$\lim_{n\to\infty} \text{REPA} = [(4/\pi) \cos (f\pi/2) + 0.5350f - 1.2680]\beta \quad \text{(A13)}$$

This limiting REPA has a maximum of $+0.051\beta$ at $f = 0.17$ and drops to 0 at $f = 0$ and to -0.733β at $f = 1.0$.

Isotope Selective Soft Multiphoton Ionization and Fragmentation of Polyatomic Molecules

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Abstract: The two-dimensional character of resonance-enhanced multiphoton ionization in a mass spectrometer is utilized for extracting a trace spectrum from the natural isotopic mixture of benzene molecules. ^{13}C labeled benzene molecules are selectively laser ionized and finally fragmented with visible laser light. The isotope selectivity obtained in the ionization process is preserved in the following fragmentation process.

Focused (10^7 W/cm^2) visible laser light can be employed to efficiently ionize molecules in the ion source of a mass spectrometer[1] if absorption proceeds via a real intermediate state. If the intensity is further increased to some 10^9 W/cm^2 a very efficient fragmentation[2] of the molecular ions is observed, finally leading to atomic ions.[3] The mechanism of this ionization and fragmentation process has been investigated in our previous work[4] and it was shown that, at least for the case of benzene, molecules first climb a ladder of the neutral molecule that barely leads to ionization of the molecules and then switch to a process in which all further absorption leads to climbing a ladder of ions. Under suitable experimental conditions[5] it is possible to avoid the fragmentation process and to achieve highly efficient "soft" ionization of a series of molecules which allows a sensitive detection of a parent molecular ion within a mixture.[5,6] In the "soft" ionization process two or three photons at most are absorbed via a real intermediate state of the molecule until the ionization potential is reached. In this case molecules are ionized by climbing only the first ladder of neutrals, the intensity being too low to lead to substantial climbing of the subsequent ion ladder. As there is a resonance condition via an intermediate state this type of ionization is particle selective to a high degree.

Even in the case of large molecules it enables one to selectively ionize particular molecules within a mixture, by employing different wavelengths.[7] In this work we shall demonstrate the high particle selectivity of a stepwise two-photon ionization by focusing on the small amount of ^{13}C labeled benzene molecules contained within a natural mixture. We shall further show that a subsequent fragmentation process does not degrade the isotope selectivity obtained in the preceding ionization process via the resonant intermediate states.

Experimental Results and Discussion

The experimental set up has been described in detail in previous work.[6] As an exciting light source we used a nitrogen pumped tunable dye laser. During this experiment an intracavity etalon was placed within the laser resonator which was pressure scanned over a wavelength range of 13 cm^{-1}. Then the laser light was frequency doubled and the UV light so produced was focused into an effusive beam of benzene molecules. The ions were withdrawn with suitable ion optics, mass analyzed in a quadrupole mass filter, and finally recorded with an ion multiplier.

Two different types of scans are possible in the mass spectrometer when measuring the ion current. The first is a wavelength scan of the dye laser at a fixed mass and the second a mass scan at different fixed laser wavelengths.

As a result, in Figure 1a the intermediate state spectrum in the two-photon ionization process is shown, when the laser

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