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Extension and Completion of the Periodic Table

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In spite of—or because of—its everyday familiarity, the periodic table possesses a number of puzzling and infrequently addressed features. (1) What is the origin of its diagonal line separating metals from nonmetals? (2) It is far from periodic: it has long been recognized that as one descends a group in the p-block the character of the elements becomes increasing metallic. The chemistry of carbon is quite different from the chemistry of lead. (3) Why do the fluorides of N, O, F, Cl, Br, He, Ne, Ar, and Kr not reach oxidation states equal to the number of their valence electrons? (4) It is our principal guide in anticipating which of the three types of bonding, covalent, metallic, or ionic, will form between atoms. But it provides no definition of these bond types, nor a way to differentiate between them. (5) It is the most powerful instrument for organizing chemical phenomena but it does not contain any information about the energy of atoms, even though everyone knows that energy is the central parameter for describing the structure of matter.

It is clear that something is missing, and this appears to be an historical accident dating from the time when Bohr provided the physical underpinning of the periodic table by defining electronic configurations.[1] In chemical terms, the periodic table is a sequence of groups whose atoms have common properties and behavior, and since a two-dimensional array displays all of the atoms, it superficially appears complete. Physicists, however, see it as a collection of valence electron configurations that depict the properties of atomic shell structure. The quantum numbers n and l introduced by Bohr[1] label blocks of elements and indicate orbital size and shape, but their primary role is to specify *energy*. When orbital occupancy is taken into account, it immediately follows that configuration energy (CE), the average one-electron valence shell energy of a ground-state free atom, is the missing third dimension:

$$\mathrm{CE} = (a\epsilon_s + b\epsilon_p)/(a + b) \qquad (1)$$

where a, b are occupanices and ϵ_s, ϵ_p the s and p ionization potentials for spherical atoms of the representative elements; for the d-block transition elements, $\epsilon_p \rightarrow \epsilon_d$ of the $n - 1$ shell and b is its valence region occupancy.[2-4] CE possesses another energy level related property that is of equal importance to that expressed in eq 1: it is strongly correlated with the spacings of the one-electron energy levels of the atom in question. Large CE goes with large energy level separations, thus making a close connection between the magnitude of CE and the density of states in solids and molecules.[4] This correlation follows immediately from the fact that the effective potential seen by an electron in an atom is funnel-shaped: steeper and deeper funnels have more widely spaced energy levels.

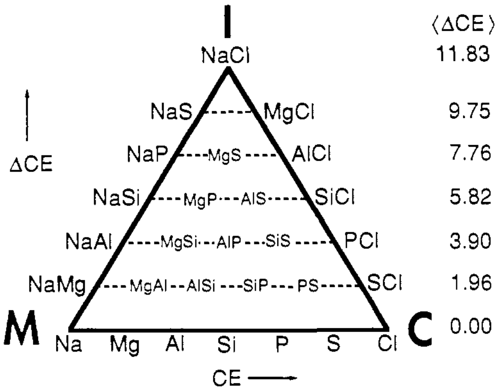

Figure 1. Quantification of a Van Arkel–Ketelaar triangle illustrated by second row atoms: M, metallic; I, ionic; C, covalent. The horizontal axis is the $n = 3$ row of the periodic table and spans a CE range from 5.14 (Na) to 16.97 eV (Cl). ⟨ΔCE⟩ is the average CE difference for pairs of atoms in each horizontal line through the triangle (the stoichiometry of the generic binary combinations of atoms has been suppressed). (The smaller size of lettering inside the triangle was employed for pictorial clarity and has no chemical significance.)

CE answers the questions posed earlier. (1) Values generated by eq 1[2,3] precisely define the metalloid band (B, Si, Ge, As, Sb, and Te) associated with the metal/nonmetal diagonal line: all elements to the right of the metalloids have higher CEs and are nonmetals; all those to the left have lower CEs and are metals. The band itself is a region of nearly constant CE. (2) Metalization down a group occurs because the size of the atoms is increasing; therefore, both the magnitude of the average valence energy level and the spacings of the levels are decreasing. Bonding directionality is being lost because the s, p, and d levels are becoming nearly degenerate, allowing mixing in many combinations. These changes are quantified by CE[4]. (3) The oxidation-state limitations of N, O, F, Cl, and Br are explained by their CEs: these and the noble gas atoms He, Ne, Ar, and Kr have the highest CEs in the periodic table and some fraction of their valence electrons is held too tightly to engage directly in bonding. Because of their high CEs, they have a correspondingly large energy gap to the first available unoccupied level, likewise discouraging bonding. (4) Quantification of Van Arkel–Ketelaar triangles[3,5] by CE and ΔCE helps interpret what the periodic table is telling us and permits one to differentiate metallic, ionic, and covalent bonding (Figure 1). Particularly interesting materials are found near the centers of each leg of the triangle: the metalloids (as well as III–V and II–VI semiconductors) along the M–C leg, polymeric compounds (e.g., AlF_3) along I–C, and Zintl phases along M–I.

It is the hypothesis of this communication that CE uniquely qualifies as an intrinsic third coordinate which completes the periodic table. A principle function of the periodic table has always been to present a two-dimensional array against which many properties have been correlated. These include the following: atomic radii,[6] polarizabilities, ionization potentials, acid–base behavior, electronegativities, boiling and melting points, diamagnetic susceptibilities, magnetic moments, field gradients at the nucleus, crystal structures, electrical and thermal conductivities, semiconductor energy gaps, etc.[7] Many of these have been presented pedagogically in texts as periodic table third dimensions, but they are actually part of its vast collection of correlative

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(1) Bohr, N. *Nature* **1923**, *112*, 29.

(2) Supplemental material attached.

(3) Allen, L. C. *J. Am. Chem. Soc.* **1989**, *111*, 9003. The new viewpoint presented here is an extension and generalization of the 1989 article.

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(6) Radius can be shown to be inversely proportional to CE.[4]

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relationships, and as demonstrated above, none except CE can claim an intimate association as a basic coordinate of the table.

Historically, the need for configuration energy has been partially met by the concept of electronegativity, originally defined by Pauling 10 years after Bohr's contribution.[8] This concept has been the subject of much debate over many years, but a survey of textbooks and the research literature since 1932 shows that only two scales, those of Pauling[8,9] and of Allred and Rochow,[10] have been extensively used by experimental scientists. We have previously shown that eq 1 closely matches these two,[3] thus assuring that the information content of electronegativity is subsumed in CE. Since CE is a simpler, more general[4] quantity and since it is an inherent part of the periodic table rather than an ad hoc independent property, it is no longer necessary to retain electronegativity per se.[11]

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Supplementary Material Available: A tabulation of configuration energies for 57 atoms and a plot of CE versus group number (2 pages). Ordering information is given on any current masthead page.

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A Receptor for the Enantioselective Recognition of Phenylalanine and Tryptophan under Neutral Conditions

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Molecular recognition of relevant biological targets constitutes a dynamic branch of organic chemistry. Recent work with model systems has led to a number of receptors for amino acids,[2,3] nucleic acid heterocyclic bases,[4] nucleotides,[5] and carbohydrates.[6]

Scheme I

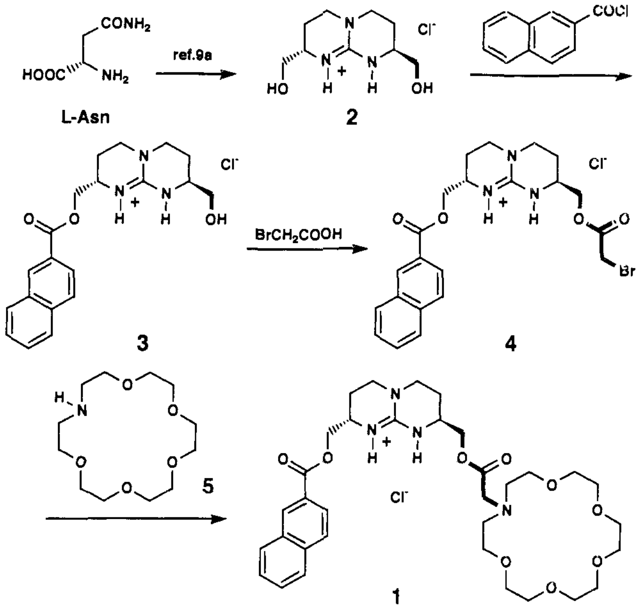

Table I. Single Extraction of a Mixture of 13 Amino Acids by Receptor **1**[a]

	total amount, μmol	ratio		total amount, μmol	ratio
Phe	2.61	100	Ala	0.09	3
Trp	1.20	46	Arg	0.05	2
Leu	0.73	28	Asp	0.05	2
Tyr	0.45	17	Pro	0.05	2
Ile	0.28	11	His	0.04	1
Gly	0.13	5	Asn	ND[b]	
Val	0.11	4			

[a] For explanation, see text and refs 14 and 15. [b] ND, not determined.

In neutral aqueous solutions, amino acids exist largely as strongly solvated zwitterionic structures. The electronic densities at the carboxylate and ammonium functions are greatly affected by their mutual vicinity, causing the binding forces of complementary groups of the receptor to be less effective for the complexation. Thus, the design of a model receptor for amino acids in zwitterionic form is still a challenging problem, and most work so far has been performed with single-charged substrates, under acidic (amino acid or amino ester salts)[2a] or basic (carboxylate salts)[7] conditions.[8] We describe herein the preparation and properties of compound **1**, a receptor for amino acids featuring the following: (i) non-self-complementary binding sites for carboxylate (a guanidinium function) and ammonium (a crown ether), preventing the receptor from internal collapse; (ii) an aromatic planar surface (the naphthalene ring) for an additional selective stacking interaction with the side chain of aromatic amino acids; (iii) a chiral structure (*S*,*S*-isomer shown) for enantioselective recognition.

The synthesis of **1** was achieved in three steps (Scheme I) from the chiral bicyclic guanidine salt **2**, readily available in optically pure form from L-asparagine.[9] Condensation with 2-naphthoyl

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