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A Theoretical Study of the Dodecahedrane Molecule

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Abstract: The molecule dodecahedrane is studied from the viewpoints of group theory, graph theory, and molecular orbital theory. A number of physical properties are considered, among them the multipole moment of the charge density, the molecular force field, and the ordering of the orbital energies. A graph-theoretic procedure for enumerating the substitutional isomers is described, and several particular cases are considered.

I. Introduction

An interesting, though relatively little-studied, class of molecules is the C_nH_n hydrocarbons whose carbon skeletons form convex polyhedra. A subset of these, the regular polyhedral hydrocarbons based upon the perfect solids of antiquity, is composed of three potential members: tetrahedrane ($n = 4$), cubane ($n = 8$), and dodecahedrane ($n = 20$)[2] (Figure 1). As yet, only cubane has been synthesized[3] and geometrically characterized.[4] Tetrahedrane has been the subject of a recent theoretical study[5] which predicted that it would be a bound molecule, detectable and perhaps amenable to isolation at low temperatures. The present paper gives the results of a theoretical study of dodecahedrane.[6,7]

Dodecahedrane is of interest because of its high symmetry, its topology, and, of course, its aesthetic allure.[8] It might well serve as a model system for many physical-organic studies, because of its rigid, though relatively strain-free structure, its limited facility for solvation, and its surface as a potential template for studying various hydrocarbon reactions. In sections II and III respectively we consider various aspects of dodecahedrane's symmetry and topology. Section IV contains the results and interpretation of a molecular orbital calculation, including a plot of the valence-electron charge density.

II. Considerations of Symmetry

One of the most striking of the symmetry properties of dodecahedrane is its sphericality (Figure 1). With CC bond lengths of 1.54 Å (the diamond distance), 20 carbons lie on a sphere of diameter 4.32 Å; the hydrogens at a bond length of 1.09 Å (the ethane value) lie on an outer sphere of 6.50 Å. In fact, dodecahedrane would be the molecule of highest known point group symmetry, I_h,[9] with 120 point group operations leaving the molecule invariant. The dodecahedrane charge density has as its first nonvanishing multipole moment the 2^6-pole moment[10]

$$\int \psi^* \gamma^6 \psi d^*\tau \tag{1}$$

where ψ is the ground state vibronic wave function and the multipole operator γ^6 is the sum over electrons and nuclei[11]

$$\gamma^6 = \sum_i q_i r_i^6 \left[\sum_{m=-6}^{6} \frac{(6-|m|)!}{(6+|m|)!} P_6^m (\cos \Theta_i) e^{im\phi} \right] \tag{2}$$

where q_i is the charge of particle i and (r_i, Θ_i, ϕ_i) are its polar coordinates referred to some suitably-chosen coordinate system with origin at any point in space; in I_h symmetry only one of the 13 nonvanishing components of the 2^6-pole tensor is unique. By contrast, the two preceding regular polyhedral hydrocarbons tetrahedrane (T_d) and cubane (O_h) have 2^3-pole (octopole) and 2^4-pole (hexadecapole) moments, respectively.

The lack of any low multipole moments in dodecahedrane implies the almost-complete absence of contributions of all but dispersion forces to the long-range interactions, e.g., to the second virial coefficient,[12] suggesting that dodecahedrane in the vapor phase will resemble a large rare gas molecule in its physical properties. For the same reason, dodecahedrane may also be anticipated to sublime more readily than would be expected for a molecule of its molecular weight. An analogous case is cubane which has a heat of sublimation of 19.2 kcal/mol at 298°K, one-fourth the value of its lower-symmetry isomer cyclooctatetraene, 71.1 kcal/mol.[13]

The high symmetry of dodecahedrane serves to simplify the description of its molecular force field. The number of independent harmonic force constants is 74, almost 100-fold fewer than the 6555 which would be necessary to characterize a completely asymmetric 40-atom molecule. This drastic reduction in independent parameters arises from the high degeneracies of the vibrational modes. The 114 normal modes belong to symmetry species: $2A_g$, T_{1g}, $2T_{2g}$, $4G_g$, $6H_g$, $3T_{1u}$, $4T_{2u}$, $4G_u$ and $4H_u$, where the T, G, and H modes are three-, four-, and fivefold degenerate, respectively (there is no twofold degeneracy in I_h symmetry). There are only three infrared active modes (T_{1u}) and eight Raman active modes ($2A_g$ and $6H_g$) and, of course, only single proton and ^{13}C NMR resonances.

It is interesting to note that dodecahedrane is a molecule almost devoid of angle strain. The CC bonds, being edges of

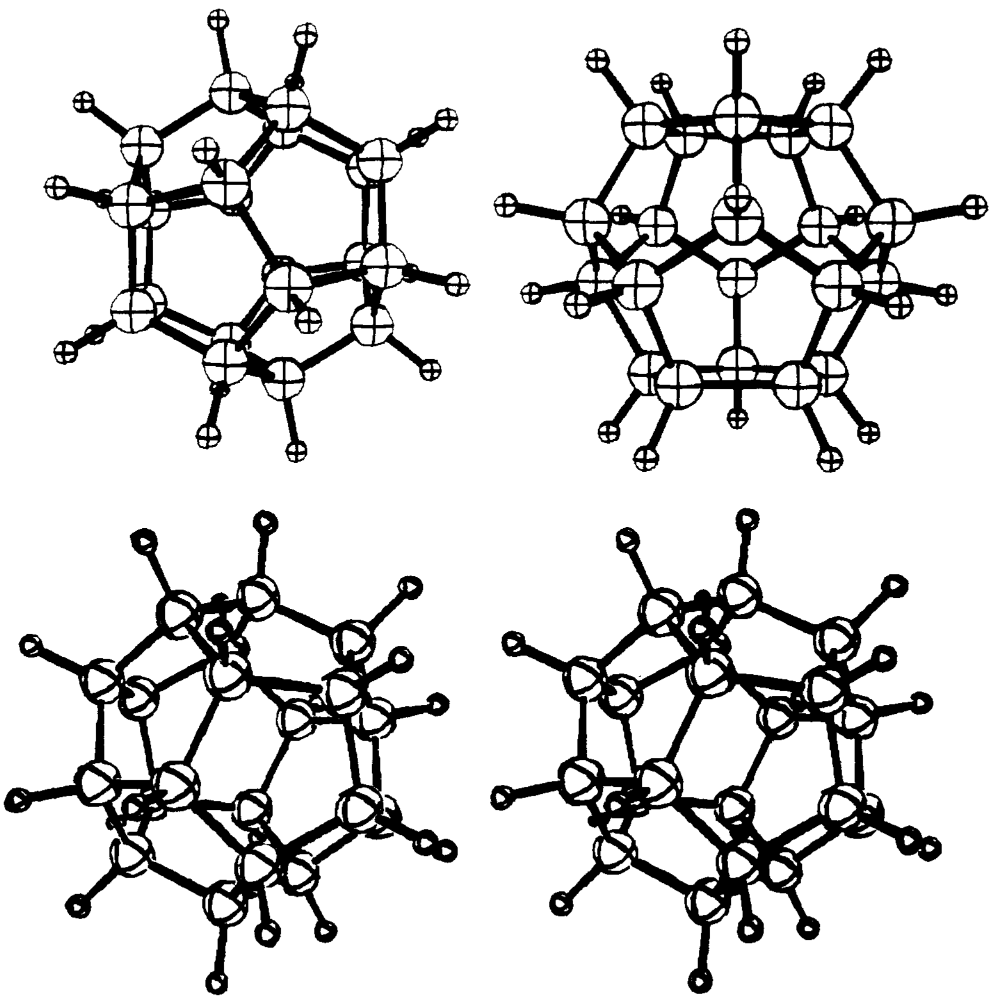
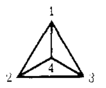


Figure 1. Three views of dodecahedrane. The bottom two are a stereoscopic pair.

regular pentagons, meet at angles of 108°; the HCC angles are calculated to be 110°54′.[14] The proximity of these angles to the idealized tetrahedral value, 109°28′, is truly remarkable, and it is anticipated that the 50 dodecahedrane bonds will very nearly coincide with their interatomic vectors and be nominally sp^3. On the other hand, there do exist numerous nonbonded interactions, for example, 30 pairs of eclipsing CH interactions, and these have been shown by empirical force-field calculations to be the dominant contributions to the steric strain in dodecahedrane.[15] Still in all, the total strain energy has been estimated to be between 43 and 88 kcal/mol at 25°,[15] implying a miniscule 2-4 kcal/mol per CH group or 1.3-3 kcal/mol per CC framework bond. Cubane and tetrahedrane have calculated strain energies of 14 and 22-24 kcal/mol, respectively, per CC bond.[5,15]

III. Considerations of Topology

The labeled graphs of the carbon skeletons of tetrahedrane, cubane, and dodecahedrane are shown below. Each is a planar graph, i.e., may be imbedded on the surface of a sphere,[16] and each region (including the exterior) arises from a polyhedron face, each vertex or node from a trivalent carbon, and each edge from a CC bond. The Euler polyhedron formula[17] (the "phase rule of topology") $v + f - e = 2$ applies to all convex polyhedra and thus serves to relate the numbers of regions, vertices, and edges of their graphs, specifically here, the graphs I-III. For dodecahedron we have $v = 20, f = 12$, and $e = 30$.



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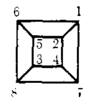

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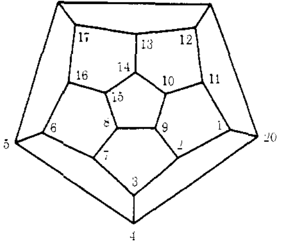

III

The graphs I-III are cubic, meaning that there are three edges incident on each vertex, and each is also hamiltonian which, by definition, requires the existence of a spanning cycle[18] (a closed, alternating sequence of vertices and edges beginning and ending with a vertex, in which each edge is incident with the vertices preceding and following it, each vertex and edge being distinct and each vertex being included in the sequence). By following the numbering in labeled graph III a spanning cycle is traversed. It may be seen that whereas all the vertices are contained in the spanning cycle, $v/2$ edges are not; moreover, these missing edges cannot be incident on the same vertex. The ten excluded edges are "zero bridges", as, for example, in the IUPAC name for dodecahedrane: undecacyclo$[9.9.0.0^{2,9}.0.^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$eicosane,[19] where the numbering is that of III and Figure 2.

An important application of graph theory to dodecahedrane is the enumeration of its substitutional isomers. The necessary graph counting methodology has been developed by Redfield[20a] and Pólya[20b] and applied to inorganic systems by Kennedy et al.[21] The basic argument utilizes the cycle index, Z, for the icosahedral group in a basis of the 20 carbon vertices which are permuted under the pure rotations of that group.

$$Z(I,\mathrm{C_{20}H_{20}}) = \frac{1}{60}\,[f_1{}^{20} + 24f_5{}^4 + 20f_3{}^6 f_1{}^2 + 15f_2{}^{10}] \quad (3)$$

Here, 60 is the order of the group and the meaning of the variables f_j raised to the ith power (i.e. $f_j{}^i$) is made clear by considering the term $20f_3{}^6f_1{}^2$ where 20 is the number of operations in the class C_3. The operations of this class leave two points invariant (hence $f_1{}^1 \cdot f_1{}^1 = f_1{}^2$) while permuting six sets of three points among themselves ($f_3{}^1 \cdot f_3{}^1 \ldots = f_3{}^6$). With the cycle index obtained it is straightforward to determine the number of stereoisomers for any substitution pattern on the dodecahedron. Consider n_k substituents of type k and m types where $\sum_k{}^m n_k = 20$. Then, replace each $f_j{}^i$ with $(x_1{}^j + x_2{}^j + \ldots x_m{}^j)^i$ in $Z(I,\ \mathrm{C_{20}H_{20}})$ and collect terms to obtain the coefficient of $x_1{}^{n_1}x_2{}^{n_2} \ldots x_m{}^{n_m}$, which is the desired number of isomers. Thus, the number of monochloromonomethyldodecahedranes is determined by the substitution $(x_1{}^3 + x_2{}^3 + x_3{}^3)^6\ (x_1 + x_2 + x_3)^2$ for $f_3{}^6f_1{}^2$, for example, and the coefficient of $x_1{}^{18}x_2x_3$ is found to be 7. This may be verified by noting that there are one one-bond, two two-bond, two three-bond, one four-bond and one five-bond substitution isomers. The two two-bond derivatives are an enantiomeric pair, e.g., the 1-methyl-3-chloro isomer is enantiomeric with the 1-chloro-3-methyl isomer (but rotationally equivalent to the 1-chloro-4-methyl derivative, the latter being considered a two-bond rather than a three-bond isomer). Similarly, the two three-bond derivatives are an enantiomeric pair, e.g., 1-methyl-5-chlorododecahedrane and 1-chloro-5-methyldodecahedrane.

The existence of enantiomers among the stereoisomers may be demonstrated by considering the cycle index of the point group I_h which includes all the group operations above and beyond the pure rotations, i.e., inversion, reflections, and improper rotations. Counting the isomers with this cycle index will not distinguish between enantiomers, which are stereoisomers nonsuperimposable by rotation just because of the fact that these S_n operations do not apply. Thus, with

$$Z(I_h,\mathrm{C_{20}H_{20}}) = \frac{1}{120}\,[f_1{}^{20} + 24f_5{}^4 + 20\,f_3{}^6f_1{}^2 + 16f_2{}^{10} + 24f_{10}{}^2 + 20f_2{}^1f_6{}^3 + 15f_1{}^4f_2{}^8] \quad (4)$$

the coefficient of $x_1{}^{18}x_2x_3$ is found to be 5, indicating that there are $7 - 5 = 2$ pairs of enantiomers. It is obvious that the benefits of this isomer counting technique accrue rapidly with increasing complexity of the substitution pattern.

Two other substitutional isomers merit particular mention. If eight of the hydrogens are replaced by eight identical ligands, e.g., chlorines, at positions (1, 7, 14, 18) and (4, 9, 12, 16), there results an example of a rigid molecule of T_h symmetry which is an exceedingly rare event. (Again, this group might preferably be named T_i as it is the direct product of the group T with the inversion operator and furthermore does not contain a reflection plane perpendicular to a threefold axis.) It might be noted that these ligands occupy the corners of a hypothetical cube inscribed within the dodecahedron. If instead of replacing eight hydrogens, only four identical ligand substitutions are made, using the sites in either the first or second parentheses, two enantiomeric molecules of the optically active point group T (i.e., a group with no improper rotations) are obtained. Again, rigid molecules of this symmetry are very rare.

IV. Molecular Orbital Theory

In this section we consider the molecular orbital description of dodecahedrane. Although the 100 valence electrons and 40 atoms precluded an ab initio treatment, a semiempirical INDO calculation was practicable, and the results are given here.

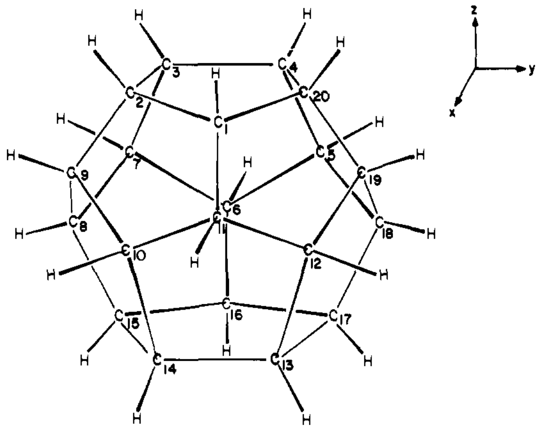

Figure 2. Depiction of the dodecahedrane molecule. The numbering of the carbon skeleton is such as to indicate a spanning cycle and corresponds to the labeled graph III.

Table I. Orbital Energies of Dodecahedrane (au)[a]

Orbital	Energy	Orbital	Energy
$1a_g$	−2.37	$2t_{2u}$	−0.59
$1t_{1u}$	−1.94	$3h_g$	−0.56
$1h_g$	−1.54	$1h_u$	−0.52
$2a_g$	−1,24	$2g_u$	−0.50
$2t_{1u}$	−1.18	$2g_g$	−0.45
$1g_u$	−1.14	$3a_g$[b]	+0.24
$1t_{2u}$	−1.02	$3t_{2u}$	+0.25
$1g_g$	−0.87	$3t_{1u}$	+0.25
$2h_g$	−0.82	$3g_g$	+0.27
		$4h_g$	+0.30

[a] INDO values for CC and CH bond lengths of 1.54 and 1.09 Å, respectively. [b] Lowest unoccupied molecular orbital.

A determination of which molecular orbitals are occupied in dodecahedrane can be made without resort to calculation, which is required only for the relative ordering. The 30 CC bonds may be considered to arise from localized molecular orbitals (LMO's) which form a basis for a_g(R), g_g, h_g(2), t_{1u}, t_{2u}, g_u, and h_u(N) canonical molecular orbitals. The designations R and N indicate species in which rigorous specification of the MO as being constructed exclusively from radial atomic orbitals or hybrids (H 1s, C 2s, C 2p) or nonradial (i.e., tangential) hybrids (C 2p) is possible. This classification applies also to the highest occupied MO of tetrahedrane (1e, N) and three occupied orbitals of cubane ($1e_g$, N; $1a_{2u}$, R; $1t_{2u}$, N) and it is, of course, a useful device for constructing symmetry-adapted basis functions in planar, cyclic systems. The 20 CH bonds or LMO's of dodecahedrane form a basis for a_g(R), g_g, h_g, t_{1u}, t_{2u}, and g_u MO's. Thus, the totality of occupied molecular orbitals should be a_g(2), t_{1u}(2), t_{2u}(2), g_g(2), g_u(2), h_g(3), and h_u(1).[22]

The intuited ground state configuration was confirmed by the occupied orbitals obtained in the INDO calculation and are given in Table I. Included in the list are the lowest few unoccupied MO's. In accounting for the relative ordering of the levels we might first note that the diagonal INDO Fock matrix elements over CC and CH LMO's are of a similar order of magnitude, as are the off-diagonal elements between pairs of CC and CC and CH LMO's incident on the same carbon. Thus, there is anticipated an interspersal of framework and CH orbital energies and, to some extent, loss of the distinctions of pure framework and

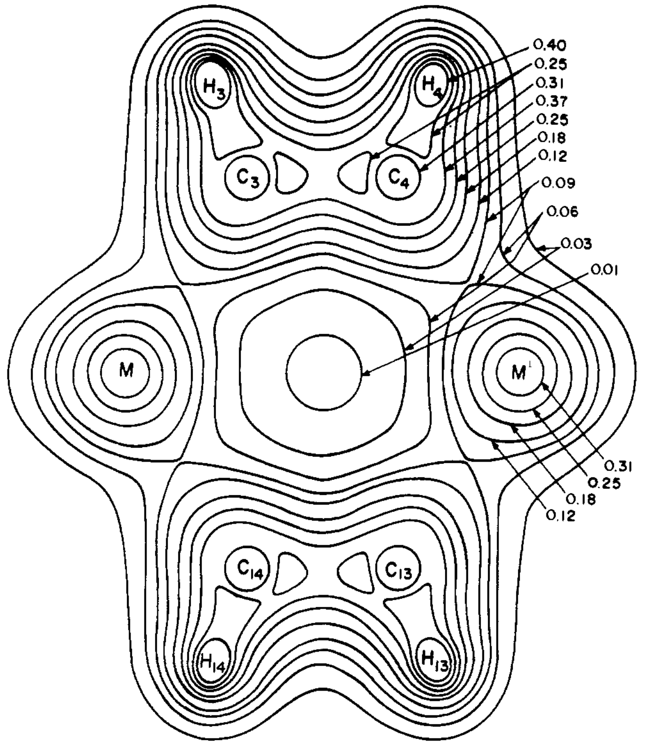

Figure 3. A charge density contour plot of dodecahedrane in a plane containing carbons C_3, C_4, C_{13}, C_{14}, the attached hydrogens, the midpoints of bonds C_8C_9 and $C_{18}C_{19}$ (M and M′), and the molecular midpoint. The charge density was constructed from the INDO density matrix and Slater orbitals according to eq 5. The same contour is obtained in the plane $y = 0$.

CH character[7] (except for the h_u orbitals, which are purely framework). The equivalent importance of CC and CH mixing also implies that no simple perturbative argument based on zeroth-order framework orbitals, with CH bonding treated as a perturbation, will suffice.

A helpful device for rationalizing the orbital ordering is the so-called crystal-field argument employed previously by Hoffmann and Gouterman[23] for some smaller polyhedra of boron and carbon atoms. The effective potential experienced by electron i in the orbital in question, arising from the 40 nuclei and remaining electrons, is assumed to be expandable in a Legendre series about the molecular center as origin. The spherically symmetric part of this effective potential furnishes a one-electron hamiltonian $h_0(i) = -\nabla_i^2/2 - Z_{\mathrm{eff}}/r_{i\rangle}$ where Z_{eff} is an effective nuclear charge and $r_{i\rangle}$ is equal to R_C, the radius of the carbon sphere (i.e., the potential is constant) for $r_i < R_C$, and $r_{i\rangle} = r_i$ for $r_i > R_C$. The orbital energies in this potential are known, from the work of Wannier[24] and Chen,[25] to be ordered in increasing energy: 1s < 2p < 2s = 3d < 3p = 4f < 3s = 4d = 5g < 4p = 5f = 6h < 5d = 6g = 7i. These orbitals transform in the group I_h according to s → a_g; p → t_{1u}; d → h_g; f → t_{2u}, g_u; g → g_g, h_g; h → t_{1u}, t_{2u}, h_u; i → a_g, t_{1g}, g_g, h_g. The ground state configuration has been intuited and confirmed by the molecular orbital calculation; thus, making the identifications that $1a_g$ arises from the 1s eigenfunction of h_0, $2a_g$ from the 2s, $1t_{1u}$ from 2p, etc., and assuming that the zeroth-order separations are larger than the first-order splittings due to the remaining part of the $r_{i\langle}$, $r_{i\rangle}$ expansion, the anticipated ordering of molecular orbitals is: $1a_g < 1t_{1u} < 2a_g \approx 1h_g < 2t_{1u} \approx 1t_{2u} \approx 1g_u < 2h_g \approx 1g_g \approx 3h_g < 2t_{2u} \approx 2g_u \approx 1h_u < 2g_g$. This is essentially the sequence obtained by the INDO calculation.

Of course, this argument is a bit deceptive in that only those eigenfunctions of h_0 are chosen which are related to those in the actual molecular orbital configuration. The spherically symmetric potential is not picking the configuration, a priori, and its ordering, but only the latter. It might also be noted that an INDO calculation on a dodecahedrane of nitrogens (the hypothetical N_{20}) furnishes a closed shell configuration identical with that of dodecahedrane, but with a rather different ordering of the orbital energies,[26] probably due to the different extent of mixing between NN framework bonds and N lone pairs. This result suggests that the success of the crystal field argument may be to some extent fortuitous.

Figure 3 is a contour plot of the dodecahedrane INDO charge density, in a plane containing carbons C_3, C_4, C_{13}, C_{14}, and their attached hydrogens, and passing through the midpoint of the molecule and the midpoints of carbon-carbon bonds C_8C_9(M) and $C_{18}C_{19}$(M′). The charge density, $\rho(\mathrm{r})$, was constructed from

$$\rho(\mathrm{r}) = \sum_{ij} P_{ij}\chi_i(\mathrm{r})\chi_j(\mathrm{r}) \qquad (5)$$

where P_{ij} is the INDO density matrix and the χ_i are carbon 2s and 2p Slater orbitals of exponent 1.625 and hydrogen 1s orbitals of exponent 1.2. This procedure is somewhat ad hoc and not entirely consistent with the zero differential overlap approximation which would exclude from eq 5 products of atomic orbitals on different atoms. However, a more consistent calculation employing the symmetrically-orthogonalized density matrix $P' = S^{-1/2}PS^{-1/2}$ in place of P[27] in eq 5 gave the same qualitative results, mainly reducing the contour levels by ca. 25%.

The most interesting feature of the contour plot is the charge density at the center of the molecule, smaller by a factor of 60 than at the CC bond midpoints, M and M′. The reason for this is the small factor $e^{-3.25R_C/a_0}$ in the contribution to $\rho(0)$.

V. The Static Jahn-Teller Effect in the Ions of Dodecahedrane

Having considered dodecahedrane from several viewpoints we now examine the ions which would result from its oxidation to $C_{20}H_{20}^+$ and reduction to $C_{20}H_{20}^-$. While these species will probably maintain the same connectivity as dodecahedrane itself, it is of interest to investigate the highest possible symmetries resulting from solution of the static first-order Jahn-Teller problem in the limit of weak spin-orbit coupling.

Consider, for example, the ^2G_g state obtained by ionizing from the highest-occupied, fourfold degenerate $2g_g$ level. The possible subgroups attained by symmetry distortion along the active G_g vibrational modes are T_h, D_{3d}, C_{2h}, S_6, and lower groups yet. Distortions involving the H_g modes lead to symmetries D_{5d}, D_{3d}, D_{2h}, S_6, C_{2h}, and lower groups, again. Only G_g and H_g modes have first-order Jahn-Teller matrix elements in a G or H electronic manifold. Now, examining the fate of the electronic levels in these lower symmetries we find that in T_h symmetry the g_g level splits into $a_g + t_g$ and in D_{3d} symmetry g_g splits into $a_{1g} + a_{2g} + e_g$. Thus, both T_h and D_{3d} are possible candidates for the highest point group of the distorted $C_{20}H_{20}^+$. On the other hand, in D_{5d} symmetry g_g splits only into the degenerate levels $e_{1g} + e_{2g}$, and this degeneracy is not lifted until the fivefold axis is lost (ultimately, C_{2h}). Therefore the ^2G_g ion cannot be of D_{5d} symmetry.

The analysis of the ^2G_u molecule arising from ionization out of the penultimate, fourfold degenerate g_u level leads to the same result as the above case, namely, T_h and D_{3d} as possible candidates. Finally, it is found that the ^2H_u, $^2T_{1u}$, and $^2T_{2u}$ ions (cations or anions possible in the latter two cases, from Table I) are candidates for D_{5d} or D_{3d} symmetry, but not T_h.

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Decomposition Rates of Excited Reaction Complexes. Temperature and Pressure Effects in Association Reactions Involving NH_4^+, $CH_3NH_3^+$, and $(CH_3)_2NH_2^+$

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Abstract: Kinetic studies were made on clustering reactions involving NH_4^+, $CH_3NH_3^+$, and $(CH_3)_2NH_2^+$ between 250 and 400°K. The association reactions $BH^+ + B + M \rightarrow B_2H^+ + M$ ($B = CH_3NH_2$, $(CH_3)_2NH$) exhibit transitions between second- and third-order kinetics in the pressure range 0.5–2.0 Torr and the temperature range 250–400°K. The dependence of the overall forward rate constants on third-body pressure confirms the energy transfer mechanism $BH^+ + B \rightleftharpoons B_2H^{+}*$ followed by $B_2H^{+}* + M \rightarrow B_2H^+ + M$. The dissociation rate constants, k_b, of the excited complexes and their temperature dependences are [given respectively as excited complex, k_b^{350} (10^7 sec^{-1}), T dependence of k_b]: $(NH_4^+{\cdot}NH_3)*$, 220, $T^{3.2}$; $(CH_3NH_3^+{\cdot}CH_3NH_2)*$, 12, $T^{3.6}$; $((CH_3)_2NH_2^+{\cdot}(CH_3)_2NH)*$, 6.0, $T^{7.2}$. The decrease of the rate constants with increasing molecular complexity and the increase with increasing temperature are quantitatively accounted for by calculations based on an RRKM coupled quantum oscillator model.

The kinetics of the decomposition processes of excited reaction intermediates is a problem of central significance in determining the rates and results of chemical reactions. The study of reactions with well-established mechanisms can provide relatively straightforward information on decomposition rates and lifetimes of excited reaction complexes and the effects of the structure, complexity, and energy content on the decomposition rates of such species. The present paper reports the results of studies on the mechanism of clustering reactions of the ions NH_4^+, $CH_3NH_3^+$, and $(CH_3)_2NH_2^+$ and the effects of temperature and molecular complexity on the decomposition rates of the excited ion-molecule association complexes $(NH_4^+{\cdot}NH_3)*$, $(CH_3NH_3^+{\cdot}CH_3NH_2)*$, and $((CH_3)_2NH_2^+{\cdot}$