ysis.[11] Complete data or reasonable estimates are known only for reactions a, b, c, and g (the filled blocks).[12] For the experiments where the data are shown as open rectangles, the results must be corrected by subtracting $\Delta H_{22}^{\ddagger}/2$, where $\Delta H_{22}^{\ddagger}$ is the enthalpy of activation for the Ru(III)-Ru(II) self-exchange reaction.[13] From available data, $\Delta H_{22}^{\ddagger}$ is expected to be between 3 and 10 kcal/mol for the other reactions[9,10,13] and it is clear that they too will fall close to the dashed line drawn in the figure.

The data in Figure 1 are in agreement with the expected linear relationship predicted by eq 6. Similar agreement is found for eq 7 but the large uncertainties in the $\Delta S°_{12}$ values calculated from cell potential measurements make such plots almost meaningless. Although the data are limited, the slope of the line is clearly close to 1.0 as predicted and the intercept at $\Delta H°_{12} = 0$ is close to $\frac{1}{2}\Delta H_{11}^{\ddagger}$ for the $Fe(H_2O)_6^{3+/2+}$ self-exchange.

The agreement between experiment and theory shown in Figure 1 is important for several reasons. There is no longer a need to invoke a special pathway for the oxidation of $Fe(H_2O)_6^{2+}$ by the M(III) polypyridine complexes. The replacement of purely σ-bonding, small, NH_3 ligands by large, π back-bonding pyridine groups has no apparent effect on the ability of the Marcus theory and the Marcus model to account for the details of the electron transfer act. The successful application of eq 6 and 7 to the reactions reported here mean that these equations can be used to probe reactions where factors not explicitly considered in the model used to derive eq 2, 6, and 7[7] may be important.

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(6) $\Delta G_{12}^{\ddagger}$ is the free energy of activation of a net reaction like eq 1, and $\Delta G°_{12}$ is the overall free energy change in the medium used: $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the free energies of activation for the self-exchange reaction.

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(8) $\Delta H_{12}^{\ddagger}$ is the enthalpy of activation of a net reaction and $\Delta H°_{12}$ is the overall enthalpy change in the medium used; $\Delta H_{11}^{\ddagger}$ is the enthalpy of activation for the self-exchange reaction and similarly for $\Delta H_{22}^{\ddagger}$. R is the gas constant, k_B is the Boltzmann constant, h is Planck's constant, and Z is the collision frequency between two neutral molecules in solution which is assumed to be 10^{11} sec^{-1}.

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(12) Thermodynamic data for the polypyridine reactions with the $Fe(H_2O)_6^{3+/2+}$ couple is known at zero ionic strength. All other data were measured in 1.0 M $HClO_4$. Data are available for $Ru(NH_3)_6^{3+/2+}$ but in a different medium. The $Ru(py)(NH_3)_5^{3+/2+}$ couple is not sufficiently stable to make formal half-cell potential measurements.

(13) The $Ru(bipy)(NH_3)_4^{3+/2+}$ self-exchange rate data were estimated from a stopped-flow study of the reaction: $Ru(bipy)(NH_3)_4^{3+} + Ru(phen)(NH_3)_4^{2+} \rightleftharpoons Ru(bipy)(NH_3)_4^{2+} + Ru(phen)(NH_3)_4^{3+}$. For the reaction, $\Delta H° = 0$ and $\Delta S° = 0$ in 1 M $HClO_4$.

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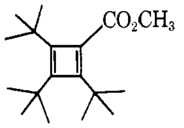
The [4]Annulene System. Direct Proof for Its Rectangular Geometry

Sir:

The central and most crucial issue of the [4]annulene system now concerns its geometry. The (presumably) most recent theoretical treatment[1] (GVB and 4-31G) of this eight-point problem concludes that the system possesses a triplet ground state of D_{4h} symmetry (square), thus conforming to the conclusion derived from the infrared analysis of the parent compound (**1**) detained in an argon matrix at 4°K.[1,2] In view of the limitations imposed upon the various methods of approximation applied to this theoretically complex molecule (**1**), it is not surprising that the above conclusion is in sharp contrast with several earlier predictions[3] that a singlet rectangle corresponds to the true minimum on the multidimensional energy surface calculated for **1**.[4] Further, there has been presented no experimental evidence against the singlet ground state *e.g.*, (i) the repeated failures to observe ESR signals that may be ascribed to the triplet,[5] (ii) the absence of allowed ultraviolet transitions above 300 nm[6] in agreement with Allinger's confident prediction[3a] for the singlet **1**, and (iii) the chemical behavior of **1** and its behavior toward dienes.[7]

An obvious and indisputable solution of this controversial problem would be a crystallographic analysis of **1**. The reactivity of **1**, however, forces us to choose for this purpose a derivative in which (i) the electronic state of **1** is least perturbed,[8] yet its reactivity is suppressed by sterically blocking the approach of another molecule by bulky substituents, thus allowing its isolation in a crystalline form, and (ii) substituents are so chosen as to preserve symmetry in an important way.[9] Our previous work[5] was aimed at the synthesis of a derivative to satisfy exactly these conditions. We have now completed an X-ray analysis of methyl tri-*tert*-butyl[4]annulenecarboxylate (**2**) and wish to record the remarkable, unambiguous outcome—**2** is definitely NOT square but a slightly distorted rectangle.

1



2

Compound **2** crystallizes by sublimation at 50° (0.01 mm) in an argon atmosphere. As these crystals were extremely sensitive to oxygen, all manipulations were carried out in a drybox under N_2. The light orange-brown plates (crystal forms present {100}, {012}, {001}) were mounted with their b axes parallel to the length of a Lindemann glass capillary which was sealed with wax. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions a = 16.796 (6) Å, b = 8.960 (3) Å, c = 12.087 (4) Å, and β = 90.76 (2)°. Intensity data were collected from a single-crystal measuring 0.30 × 1.00 × 0.57 mm with respect to the a, b, and c axes, on a Picker FACS-1 diffractometer with Cu Kα radiation to $2\theta = 120°$. A total of 2339 unique and space group allowed reflections were used in the structure solution and refinement. Corrections for Lorentz and polarization factors were made, and an empirical absorption correction[10] was applied.

The structure was solved by the application of the direct method.[11] The initial E map clearly showed the atoms of the [4]annulene ring, the non-hydrogen atoms of the methoxycarbonyl group, and two of the *tert*-butyl groups but only the tertiary carbon atom of the third *tert*-butyl group (on C(4)). The present R factor of 0.105 was obtained from a model in which all the non-hydrogen atoms were refined

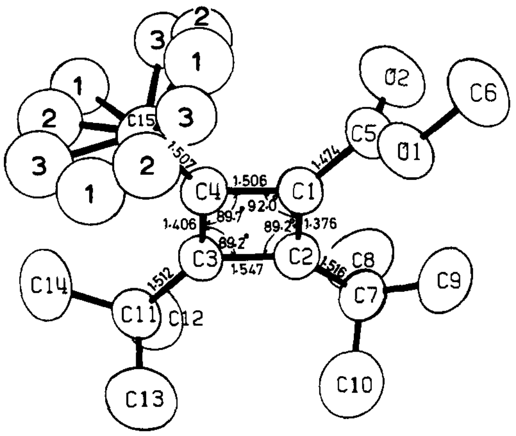


Figure 1. Methyl tri-*tert*-butyl[4]annulenecarboxylate. Selected bond distances and angles are given and the estimated standard deviations of the bond distances and angles are 0.005 Å and 0.3°, respectively. The three sites (occupancies 0.51, 0.32, 0.17) of the disordered methyl groups bonded to C15 are designated as 1, 2, and 3, respectively.

with anisotropic temperature factors, except for the three-site (relative occupancies 1 (0.51), 2 (0.32), and 3 (0.17)) disordered methyl-carbon atoms, of the *tert*-butyl group on C(4), which were refined with isotropic thermal parameters; the parameters of the 21 hydrogen atoms (located by a difference Fourier synthesis) of the other methyl groups of the molecule were held constant. A listing of anisotropic temperature factors is available; see paragraph at end of paper regarding supplementary material. Further refinement with this atom grouping described by a hindered rotor model is in progress.

An ORTEP[12] drawing of the molecule is given in Figure 1 which also shows the atomic numbering scheme and some pertinent bond distances and angles. The [4]annulene ring in this derivative is not square but, rather, more rectangular. It is quite clear that the chemically equivalent bonds C(1)-C(2), C(1)-C(4) and C(2)-C(3), C(3)-C(4) are of *unequal* length. The two short bonds C(1)-C(2) and C(3)-C(4) are within 3σ of the accepted aromatic bond length of 1.394 Å,[13] therefore definitely much longer than double bonds (1.335 Å).[13] Of the two longer bonds only C(2)-C(3) is of single bond character whereas C(1)-C(4) has a length similar to that between C sp^2 and C sp^3 (viz., C(2)-C(7), C(3)-C(11), and C(4)-C(15)).

The two bonds which are affected by the substitution are C(2)-C(3) and C(3)-C(4). They are 0.04 and 0.03 Å longer than their counterpart distances C(1)-C(4) and C(1)-C(2). In addition the exocyclic angles C(7)-C(2)-C(3) (139.9 (3)°), C(11)-C(3)-C(4) (138.1 (3)°), and C(15)-C(4)-C(3) (141.6 (3)°) are all considerably larger than the undistorted value of 135°. These distances and angles indicate some crowding of the bulky *tert*-butyl groups on atoms C(2), C(3), and C(4). Even though there appears to be overcrowding of the *tert*-butyl groups, the closest H-H approach in this conformation is 2.13 Å, not significantly shorter than a van der Waals contact of 2.2-2.3 Å expected for H atoms.

The four carbon atoms of the [4]annulene ring are strictly coplanar ($\chi^2 = 0.02$).[14] Also, the four non-hydrogen atoms of the methoxycarbonyl group are coplanar ($\chi^2 = 0.72$). The dihedral angle between the plane of this group and that of the ring is 84.1°. Steric interactions with the neighboring *tert*-butyl groups clearly impose this conformation on the C(1)-C(5) bond, thus little or no π-electron overlap from the C(5)-C(2) bond with the ring is possible. Because of the equality of the exocyclic angles C(15)-C(4)-C(1) (128.6 (3)°) and C(7)-C(2)-C(1) (130.8 (3)°) and C(2)-C(1)-C(5) (134.4 (3)°) and C(4)-C(1)-C(5) (133.3 (3)°), neighboring interactions of the methoxycarbonyl group with the *tert*-butyl groups on C(2) and C(4) are not severe and appear to be of the same order of magnitude.

Because of the substitution pattern of **2**, the two bonds C(1)-C(4) and C(1)-C(2) would be of equal length in the present case, if a square conformer were at the true energy minimum of the system. Our result represents the first clear, direct evidence to demonstrate that a rectangle, distorted slightly by the substituents, corresponds to the most stable conformation of this [4]annulene system.[15-17]

Supplementary Material Available. A listing of anisotropic temperature factors and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-1973.

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(14) The four atoms bonded to the ring are out of plane: C(5), −0.108; C(7), −0.067; C(11), 0.075; and C(15), 0.057 Å. These deviations from coplanarity, although significant, are relatively small.

(15) Repeated attempts to observe ESR signals that may be ascribed to a triplet ground state have consistently failed. In these experiments, 1 was generated under a variety of conditions (4°K, argon matrix; 90°K, organic matrix) and from different precursors. We are now almost certain that the ground state of 1 is singlet. The likely geometry of 1 is a rectangle with two short bonds appoximately 1.37 Å and two longer ones of the order of 1.51 Å.[3b] Should **1** prove to be a square for reasons that are not obvious at the present moment, both square and rectangular 1 must reside in a region of a flat potential surface.

(16) The photoelectron spectrum of **2** is recorded: R. S. Brown and S. Masamune, *Can. J. Chem.*, in press.

(17) The authors wish to thank the Medical Research Council of Canada (L.T.J.D. and M.N.G.J.) and the National Research Council of Canada (S.M. and N.N.) for financial support of this work.

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