Bis(cyclobutadiene)nickel: Geometrical and Electronic Structure

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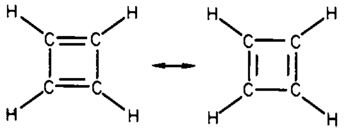
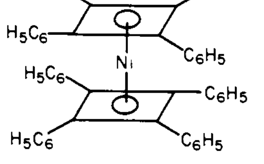
Abstract: Nonempirical molecular electronic structure theory has been used to study the $Ni(C_4H_4)_2$ molecule, which serves as a model for the recently synthesized bis(tetraphenylcyclobutadiene)nickel. Self-consistent-field (SCF) theory was used in conjunction with a large and flexibly contracted Gaussian basis set, labeled Ni(14s9p6d/10s6p3d), C(10s6p/6s3p), H(5s/3s). After preliminary investigation predicted the eclipsed (D_{4h}) conformation to lie 1.3 kcal below the staggered (D_{4d}) form, a more complete examination of the D_{4h} equilibrium geometry was undertaken. This yielded r_e(Ni–ring) = 1.722 Å, r_e(C–C) = 1.453 Å, and a CH bend back angle (relative to the plane of the four carbon atoms) of 5.2°. In comparison, the C–C distance in isolated square ($^3A_{2g}$ state) cyclobutadiene is predicted to be 1.438 Å by analogous theoretical methods. The ionization potentials of $Ni(C_4H_4)_2$ are predicted both from Koopmans' theorem and direct hole state calculations. These results are used in conjunction with Mulliken populations to discuss the electronic structure of $Ni(C_4H_4)_2$ in a qualitative way.

The story of cyclobutadiene forms an interesting chapter in the history of organic chemistry.[1,2] A similarity with the aromatic benzene molecule is implicit in the equivalent valence structures


(1)

but efforts prior to 1960 to synthesize cyclobutadiene were fruitless. However, later developments proved the reasonableness of the 1956 proposal of Longuet-Higgins and Orgel,[3] in a paper titled "The Possible Existence of Transition-Metal Complexes of Cyclobutadiene". There they pointed out that while the cyclopentadienyl radical C_5H_5 is relatively unstable, sandwich compounds such as ferrocene are very stable. By analogy Longuet-Higgins and Orgel argued that although cyclobutadiene itself had never been made, a molecule such as $Ni(CN)_2(C_4H_4)$ might prove to be rather stable. The qualitative theoretical ideas of Longuet-Higgins and Orgel[3] were vindicated in 1965 when Pettit and co-workers[4] prepared the cyclobutadiene iron tricarbonyl molecule $(C_4H_4)Fe(CO)_3$. Since then, of course, the naked C_4H_4 molecule has been synthesized without the use of transition metals.[1]

Perhaps an even more striking demonstration that cyclobutadiene (CBD) is stabilized by transition metals is the recent synthesis of the first CBD sandwich compound, bis(tetraphenylcyclobutadiene)nickel


(2)

Hoberg, Krause-Göing, and Mynott[5] found that $Ni(C_4Ph_4)_2$ crystallizes as small well-formed blue needles, with a melting point of 404 °C, and is relatively unreactive. For example, the ligands cannot be replaced by CO, even at 110 °C and 1 atm, and the compound is both air stable and unaffected by boiling water. All these observations point to a well-protected nickel atom for which the 18 electron rule[3,6] is satisfied.

At such an early stage in the development of CBD sandwiches, it is not surprising that the unsubstituted $Ni(C_4H_4)_2$ has not yet been reported. It should be noted that the phenyl substituted $(C_4Ph_4)Fe(CO)_3$ compound was prepared[7] 6 years before the unsubstituted $(C_4H_4)Fe(CO)_3$. Further, Pettit has noted[2] that there is "no obvious reason why the four (phenyl) substituents should play an important role in the bonding scheme", and this is equally true for $Ni(C_4Ph_4)_2$. Of course, while the bonding in $Ni(C_4H_4)_2$ should be very similar to that in $Ni(C_4Ph_4)_2$, the phenyl substituents do protect the nickel atom and greatly reduce its reactivity relative to the unsubstituted molecule.

Here we present a detailed theoretical study of the prototype CBD sandwich compound $Ni(C_4H_4)_2$. This study is relatively unique in that it is one of a small number[8,9] in which theory approaching the Hartree–Fock level has been used to study the geometrical structure of organotransition-metal species. Since a crystal structure of $Ni(C_4Ph_4)_2$ should be forthcoming, comparison should be of interest. Certain parameters, such as the tilt angle of the C–H bonds relative to the C_4 plane, are probably better determined at present by theory than by experiment. Finally, it should be of interest to compare the present quantitative ab initio picture of the electronic structure of $Ni(C_4H_4)_2$ with traditional qualitative ideas, exemplified by Figure 1, redrawn from a recent text[10] on group theory in chemistry.

Theoretical Approach

Assuming an analogy between $Ni(C_4H_4)_2$ and the cyclopentadienyl sandwiches[11] $M(C_5H_5)_2$, with M = transition metal,

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(1) S. Masamune, *Pure Appl. Chem.*, **44**, 861 (1975); T. Bally and S. Masamune, *Tetrahedron*, **36**, 343 (1980).

(2) R. Pettit, *J. Organomet. Chem.*, **100**, 205 (1975).

(3) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc., London*, 1969 (1956).

(4) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965). See: A. Efraty, *Chem. Rev.*, **77**, 691 (1977), for a review of cyclobutadienemetal complexes.

(5) H. Hoberg, R. Krause-Göing, and R. Mynott, *Angew. Chem., Int. Ed. Engl.*, **17**, 123 (1978).

(6) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

(7) W. Hubel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **10**, 250 (1959); the other early (chronologically) CBD complex was the (tetramethylcyclobutadiene) nickel chloride dimer, prepared by R. Criegee and G. Schroder, *Justus Liebigs Ann. Chem.*, **623**, 1 (1959).

(8) See, for example, D. Spangler, J. J. Wendoloski, M. Dupuis, M. M. L. Chen, and H. F. Schaefer, *J. Am. Chem. Soc.*, **103**, 3985 (1981). A Model Transition Metal Carbene", to be published.

(9) R. M. Pitzer and H. F. Schaefer, *J. Am. Chem. Soc.*, **101**, 7176 (1979).

(10) See pp 269 and 270 of L. H. Hall, "Group Theory and Symmetry in Chemistry", McGraw-Hill, New York, 1969.

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Table I. Basis Set of Contracted Gaussian Functions Employed in the Theoretical Study of $Ni(C_4H_4)_2$

	orbital exponent α	contraction coeff		orbital exponent α	contraction coeff
nickel			carbon		
s	284 878	0.001 581	s	9 470.52	0.001 477
	41 997.9	0.012 385		1 397.56	0.011 849
	9 627.67	0.063 037		307.436	0.063 815
	2 761.96	0.247 583		84.605 73	0.255 583
	920.488	0.751 404		26.921 79	0.747 951
s	341.805	1.0	s	9.412 992	1.0
s	138.023	1.0	s	3.479 817	1.0
s	59.258 7	1.0	s	1.071 231	1.0
s	20.371 2	1.0	s	0.400 791 5	1.0
s	8.594 00	1.0	s	0.135 166 0	1.0
s	2.394 17	1.0			
s	0.918 169	1.0	p	25.627 08	0.016 014
s	0.130 176	1.0		5.846 072	0.100 115
s	0.046 392	1.0		1.799 351	0.341 811
				0.654 332 9	0.669 585
p	1 774.18	0.007 801	p	0.248 692 1	1.0
	423.403	0.061 706	p	0.090 926 6	1.0
	138.311	0.274 733			
	53.170 3	0.745 201	hydrogen		
p	22.387 4	1.0	s	33.644 4	0.025 374
p	9.928 48	1.0		5.057 96	0.189 683
p	4.116 25	1.0		1.146 80	0.852 930
p	1.710 31	1.0	s	0.321 144	1.0
p	0.672 528	1.0	s	0.101 309	1.0
d	48.940 3	0.032 801			
	13.716 9	0.177 537			
	4.639 51	0.440 579			
	1.574 33	0.568 907			
d	0.486 409	1.0			
d	0.131 6	1.0			

there should be two nearly degenerate conformers, staggered (D_{4d}) and eclipsed (D_{4h}). In D_{4h} symmetry the ground state electron configuration for $Ni(C_4H_4)_2$ is (omitting the nickel 1s, 2s, 2p, 3s, and 3p orbitals and all the CBD orbitals except the ring π orbitals)

$$\ldots 7a_{1g}^2\ 6a_{2u}^2\ 4e_g^4\ 6e_u^4\ 8a_{1g}^2\ 3b_{1g}^2\ \ 2b_{2g}^2 \tag{3}$$

Here we have simply accepted the orbital ordering given in Hall's textbook (Figure 1), noting his apparently inadvertant omission of the a_{2u} orbital from his correlation diagram for this complex, but not of the corresponding orbital in his diagrams for other sandwich complexes. The analogous electron configuration for the D_{4d} or staggered conformation is

$$\ldots 7a_1^2\ 6b_2^2 4e_3^4\ 6e_1^4\ 8a_1^2\ 3e_2^4 \tag{4}$$

Comparison of (3) and (4) shows that the doubly degenerate $3e_2$ orbital splits into $3b_{1g}$ and $2b_{2g}$ components as one passes from the staggered conformation to the eclipsed. This is the only major qualitative difference between the electronic structures of the D_{4d} and D_{4h} conformers. The present ab initio theoretical study is primarily concerned with the closed-shell electronic states (3) and (4) and to a lesser degree with their various monopositive ions.

Notoriously large basis sets are required for reliable quantum mechanical studies of molecules containing transiton-metal atoms. Fortunately, this problem has been discussed in detail elsewhere,[12-19] and a full exposition is unnecessary here. It should be emphasized, however, that large, flexibly contracted Gaussian basis sets were used in the present study of $Ni(C_4H_4)_2$. Specifically, the "middle basis set" used by Pitzer and Schaefer[9] in their work on $Ni(C_2H_4)_3$ was adopted. This basis may be designated Ni(14s 9p 6d/10s 6p 3d), C(10s 6p/6s 3p), H(5s/3s) and is roughly of "triple-ζ" quality. The nickel basis arises from the appendage of a more diffuse (or valence like) set of d functions[16] to the standard Wachters[12] (14s 9p 5d) set. The carbon and hydrogen bases are standard contractions of Huzinaga's primitive Gaussian sets.[20] The precise specifications of the basis set are given in Table I.

All predictions reported here were obtained at the restricted Hartree–Fock or self-consistent-field (SCF) level of theory. To carry out a rigorous three-dimensional SCF geometry optimization with a contracted Gaussian basis of 187 functions is a demanding computational task, but was rendered viable in this case by the equal contributions symmetry analysis[21] developed for molecules of high point group symmetry. Basis integrals were evaluated by using the Rys polynomial method,[22] as implemented in the HONDO subroutines.

Eclipsed–Staggered Energy Difference

For the well-known cyclopentadienyl sandwich compounds, small barriers (0.9 ± 0.3 kcal/mol for ferrocene) to rotation about the fivefold axis appear to be the rule.[11] For compounds such as the known[5] $Ni(C_4Ph_4)_2$ and the prototype $Ni(C_4H_4)_2$ it is natural to inquire about the magnitude of the analogous fourfold barrier to rotation.

Our investigation of the $D_{4h} - D_{4d}$ energy difference began with geometrical structure chosen by reference to the crystal structure[23] of (1,2,3,4-tetramethylcyclobutadiene)nickel dichloride. Assumed geometrical parameters were:

$$\begin{array}{ll} r(\text{Ni–ring}) = 1.74\ \text{Å} & r(\text{C–C}) = 1.45\ \text{Å} \\ r(\text{C–H}) = 1.08\ \text{Å} & \theta(\text{H bend back}) = 10° \end{array} \tag{5}$$

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[11] A. Haaland, *Acc. Chem. Res.*, **12**, 415 (1979); S. Carter and J. N. Murrell, *J. Organomet. Chem.*, **192**, 399 (1980).

[12] A. J. H. Wachters, *J. Chem. Phys.*, **52**, 1033 (1970).

[13] B. Roos, A. Veillard, and G. Vinot, *Theor. Chim. Acta*, **20**, 1 (1971).

[14] H. L. Hsu, C. Peterson, and R. M. Pitzer, *J. Chem. Phys.*, **64**, 791 (1976).

[15] P. S. Bagus, U. I. Wahlgren, and J. Almlöf, *J. Chem. Phys.*, **64**, 2324 (1976).

[16] P. J. Hay, *J. Chem. Phys.*, **66**, 4377 (1977).

[17] B. R. Brooks and H. F. Schaefer, *Mol. Phys.*, **34**, 193 (1977).

[18] W. C. Swope and H. F. Schaefer, *Mol. Phys.*, **34**, 1037 (1977).

[19] D. M. Hood, R. M. Pitzer, and H. F. Schaefer, *J. Chem. Phys.*, **71**, 705 (1979).

[20] S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).

[21] R. M. Pitzer, *J. Chem. Phys.*, **58**, 3111 (1973).

[22] M. Dupuis, J. Rys, and H. F. King, *J. Chem. Phys.*, **65**, 111 (1976).

[23] J. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, **45**, 647 (1962).

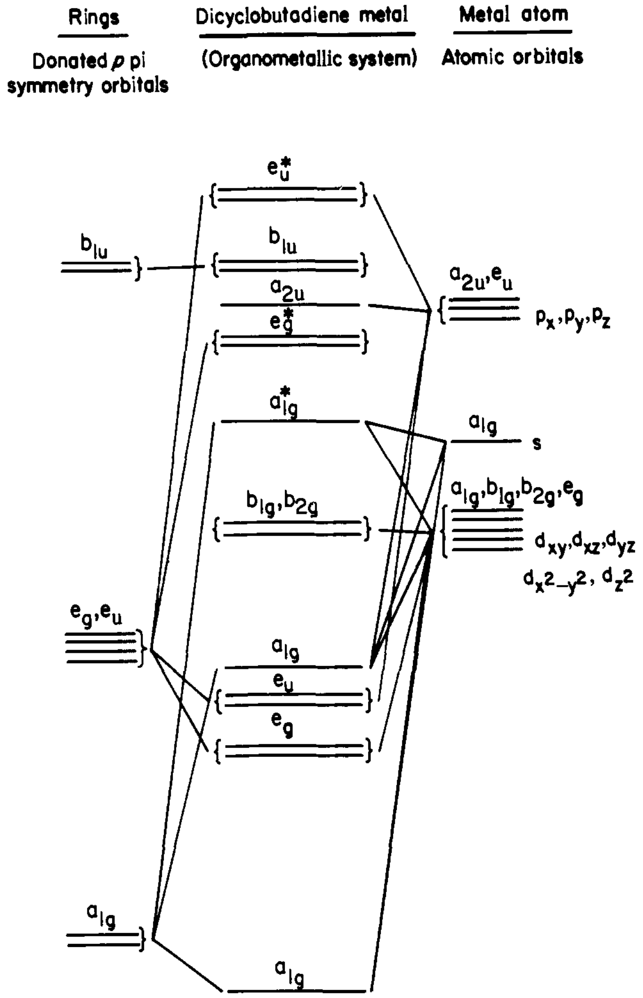

Figure 1. Qualitative molecular orbital diagram for dicyclobutadiene–metal sandwich compounds $M(C_4H_4)_2$ based on estimates of energy level spacings. This figure appears in ref 10 and has been redrawn and the orbitals relabeled to suit the conventions adopted in the present paper.

At these geometries the SCF total energies were −1813.96752 (D_{4h}) and −1813.96544 hartrees (D_{4d}), the eclipsed form lying 1.31 kcal lower.

Thus it seemed quite likely that the D_{4h} conformer of $Ni(C_4H_4)_2$ is the lower lying. Therefore, subsequent efforts were aimed primarily at the structural optimization of the D_{4h} conformation. When this optimization (to be described below) was completed, the total energy obtained was −1813.97116 hartrees. With these optimum D_{4h} geometrical parameters, a single calculation on the D_{4d} conformer was carried out and yielded a total energy of −1813.96931 hartrees. This comparison suggests and the D_{4d} geometry lies 1.16 kcal above the D_{4h} structure. Our conclusion is that the $D_{4h} - D_{4d}$ energy difference is relatively insensitive to the other geometrical parameters and is in any case about 1 kcal/mol, which is very similar to the ferrocene value.

Theoretical Equilibrium Geometry

Beginning with (5), the geometry of D_{4h} $Ni(C_4H_4)_2$ was completely optimized except for the assumption that the eight equivalent C–H distances were 1.08 Å. A satisfactory optimization of the metal–ring distance, ring C–C distance, and hydrogen bend back angle required 22 independent SCF calculations, whose geometries and total energies are available from the authors upon request. The predicted equilibrium geometry is seen in Figure 2. The final Ni–ring and C–C distances are remarkably close to those initially assumed on the basis of the known $Cl_2Ni(C_4Me_4)$ crystal structure.[23] The out-of-plane bending of the C–H bonds is, however, only about half of the initial estimate, and is opposite in direction to the observed bending angle in ferrocene.[11]

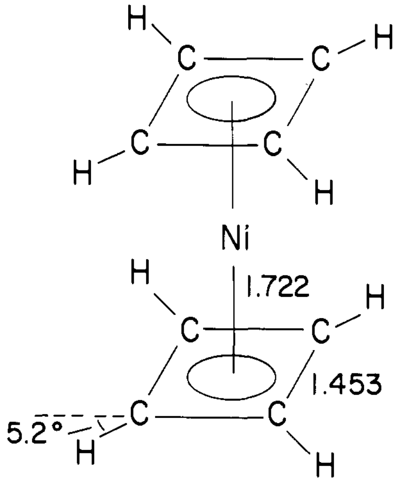

Figure 2. Predicted equilibrium geometry for the D_{4h} eclipsed conformation of bis(cyclobutadiene)nickel. The eight equivalent C–H distances were assumed to be 1.08 Å. The 5.2° angle depicts the bending of each C–H bond out of the plane of the four-carbon ring.

Table II. Gross Atomic Population via Mulliken Analysis for $Ni(C_4H_4)_2$ and Isolated C_4H_4 in Its $^3A_{2g}$ Electronic State, Which Has a Square Equilibrium Geometry

	s	p	d	total	charge
		D_{4h} $Ni(C_4H_4)_2$			
Ni	6.529	12.063	8.620	27.212	+0.788
C	3.250	3.131		6.380	−0.380
H	0.718			0.718	+0.282
		D_{4d} $Ni(C_4H_4)_2$			
Ni	6.547	12.063	8.607	27.218	+0.782
C	3.257	3.122		6.378	−0.378
H	0.720			0.720	+0.280
		$^3A_{2g}$ C_4H_4			
C	3.169	3.102		6.271	−0.271
H	0.729			0.729	+0.271

For comparison, the equilibrium geometry of the lowest square (i.e., D_{4h}) electronic state of isolated cyclobutadiene was predicted. The ground state of CBD is now established[24] to be rectangular, but the lowest triplet state, the $^3A_{2g}$ state, is square. Assuming C–H distances of 1.08 Å, the $^3A_{2g}$ C–C distance is predicted to be 1.438 Å, or 0.015 Å shorter than in $Ni(C_4H_4)_2$ (see Figure 2).

Some mention of the recent ferrocene paper by Lüthi, Ammeter, Almlöf, and Korsell[25] is required here. These workers optimized the metal–ring distance in $Fe(C_5H_5)_2$ and found it to be 1.89 Å, much larger than the experimental[26] distance, 1.65 Å. This poor agreement with experiment certainly comes as a surprise. Almlöf and co-workers used a basis set of size Fe(12s 7p 4d/8s 5p 3d), C(7s 3p/4s 2p), H(4s/2s). Such a basis set will yield much higher absolute energies than the basis used in our research, but should otherwise be quite acceptable. This appears to be confirmed by further unpublished results by Lüthi,[25] obtained with a much larger basis set, but yielding essentially the same unrealistically long metal–ring distance. Such a problem does not appear to occur in $Ni(C_4H_4)_2$, for which the present predicted Ni–ring distance is very similar to that determined crystallographically by Dunitz et al.[23] for $Cl_2Ni(C_4Me_4)$.

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(24) This is one of the relatively few cases in which theory challenged an apparently sound experimental structure and was ultimately vindicated. See O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973); W. T. Borden, E. R. Davidson, and P. Hart, *ibid.*, **100**, 388 (1978); S. Masamune, F. A. Souto-Bachiller, T. Machiguchi, and J. E. Bertie, *ibid.*, **100**, 4889 (1971).

(25) H. P. Lüthi, J. Ammeter, J. Almlöf, and K. Korsell, *Chem. Phys. Lett.*, **69**, 540 (1980), and further unpublished work.

(26) L. Hedberg and K. Hedberg, *J. Chem. Phys.*, **53**, 1228 (1970).

Mulliken Atomic Populations

Table II give gross atomic populations as defined by Mulliken[27] for eclipsed and staggered $Ni(C_4H_4)_2$ and for isolated C_4H_4. The isolated CBD results are typical of hydrocarbons in that they suggest $C^{-\delta}H^{+\delta}$ polarity, i.e., a flow of electronic charge from hydrogen to carbon upon molecule formation. Very similar hydrogen populations are seen in $Ni(C_4H_4)_2$, the "positive charges" increasing by ~0.01 Mulliken electron. However, the eight carbon atoms in the sandwich compound have taken on notably more (by ~0.11 Mulliken electron) negative populations than was the case for isolated cyclobutadiene. This results in a net Ni positive charge in the Mulliken picture of nearly 0.8. The increased C population in $Ni(C_4H_4)_2$ as opposed to C_4H_4 resides in both the carbon s and p functions with the increase in the s population being the larger of the two.

The breakdown of the nickel population into s, p, and d components is particularly interesting, since $Ni(C_4H_4)_2$ is nominally a d^{10} sandwich complex.[28] Given the positive charge of +0.8 on the Ni in the Mulliken picture, of course, one cannot possibly expect a d^{10} population to emerge. At best one might expect $d^{9.2}$, and in fact one finds $d^{8.6}$.

With the nominal d^{10} Ni atom as a beginning, a detailed examination of the charge shows that in the A_{1g} orbitals there is a ligand $\pi \rightarrow$ Ni 4s donation of 0.47 and a small 3d → 4s donation of 0.06. The largest charge flow is in the populations of the E_g orbitals where there is a 3d → π^* back-donation of 1.29. Finally, in the E_u and A_{2u} orbitals there is a small ligand → Ni 4p donation of 0.06 as well as a flow of electron population from the C p orbitals to the C s orbitals, consistent with the calculated lengthening of the CC bond distance and bending back of the CH bonds. This results in the net Ni → ligand electron donation causing a larger increase in the C s orbital population than in the C p orbital population. The overall effect on the Ni of these changes is to make its population $s^{0.53}$ $d^{8.62}$ rather than the simplified d^{10}.

By comparison with other organonickel complexes studied at this level of theory, the distribution of Ni s and p electrons is much closer to that of $Ni(C_2H_4)_3$[9] than to $Ni(CO)_4$.[8] $Ni(C_2H_4)_3$ has 0.27 4s Mulliken electron and 0.02 4p, while $Ni(CO)_4$ has 0.06 4s and 0.58 4p. However, the Ni d population of $Ni(C_4H_4)_2$, 8.62, is much closer to that in nickel–tetracarbonyl, 9.13, than to the 9.37 predicted for $Ni(C_2H_4)_3$. Comparisons of this sort must, of course, only be made when very similar basis sets are used for the different molecules in question.

The most important improvement to our $Ni(C_4H_4)_2$ wave function is anticipated to be the addition of the $6e_u^2\ 5e_g^2$ ($\pi \rightarrow \pi^*$ double excitation) configuration, which is expected to reduce the 3d → π^* back-donation to some extent, as well as improve our calculated dissociation energy. With our present Hartree–Fock wave functions, a value of 79 kcal/mol is obtained for the dissociation energy relative to d^{10} ^1S Ni and $^3A_{2g}$ CBD, but little significance should be attached to this value since Hartree–Fock wave functions are not expected to provide accurate values for dissociation energies, particularly in this case where the ligands have open-shell ground states.

Ionization Potentials of $Ni(C_4H_4)_2$ and Ordering of Molecular Orbitals

The simplest method of predicting ionization potentials within the Hartree–Fock approximation is via Koopmans' theorem, i.e., simply reporting the orbital energies. A more consistent theoretical procedure is to perform a direct SCF calculation on the pertinent positive ion state and subtract this energy from that of the neutral molecule. This method, the ΔSCF approach, has also been used in the present work. Both sets of ionization potentials are reported for D_{4h} bis(cyclobutadiene)nickel in Table III. Since the neutral complex MO's do not correspond exactly to the MO's obtained in the ΔSCF calculations, we have arbitrarily numbered the MO's by using the ΔSCF order, and made as close a correspondence as possible in labeling the neutral complex MO's.

Table III. Predicted Ionization Potentials for the Eclipsed (D_{4h}) Equilibrium Geometry of $Ni(C_4H_4)_2$

Koopmans' theorem			ΔE SCF		
orbital	character	IP, eV	orbital	character	IP, eV
$6e_u$	π	7.11	$2b_{2g}$	d	5.84
$4e_g$	d	10.83	$3b_{1g}$	d	6.17
$6a_{2u}$	π	13.26	$6e_u$	π	6.51
$1b_{2g}$	CCσ	13.99	$8a_{1g}$	d	6.61
$5e_u$	CH	14.27	$4e_g$	d	7.28
$7a_{1g}$	π	14.65	$6a_{2u}$	π	12.53
$3b_{1g}$	d	14.72	$5e_u$	CH	13.76
$1b_{1u}$	CCσ	14.79	$1b_{1u}$	CCσ	14.02
$3e_g$	CH	14.83	$3e_g$	CH	14.27
$2b_{2g}$	d	16.20	$1b_{2g}$	CCσ	14.79
$8a_{1g}$	d	16.61	$7a_{1g}$	π	14.97

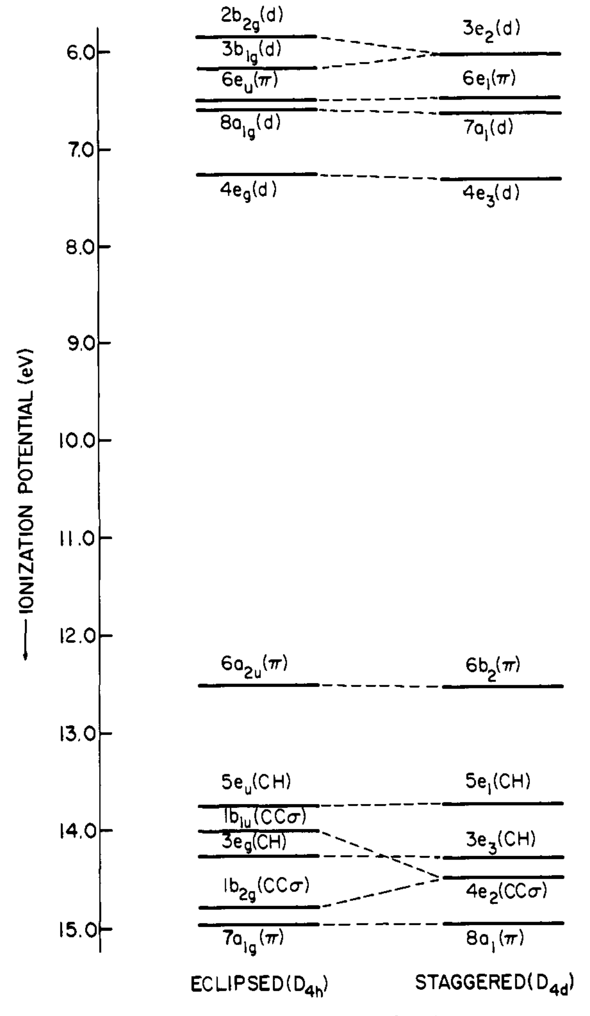

Figure 3. Theoretical ionization potentials, obtained via direct SCF calculations on each individual positive ion state, for eclipsed (D_{4h}) and staggered (D_{4d}) $Ni(C_4H_4)_2$.

Perhaps the most readily apparent feature of Table III is the magnitude of the IP relaxation energies, defined as

$$\text{IP(Koopmans)} - \text{IP}(\Delta\text{SCF}) \qquad (6)$$

The relaxation energy for a given IP is equivalently the difference between the single-configuration ion energy obtained by using the neutral molecule SCF orbitals and that obtained with the SCF orbitals optimum for that particular positive ion state. Reference to Table III shows that the neutral molecule SCF orbitals do a rather poor job of describing the ion states in which a d electron has been removed. This same qualitative result has been consistently reported for transition-metal complexes (see, for example ref 9 and 14). The larger such relaxation energies seen in Table

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(27) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833, 1841 (1955).

(28) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974.

III are for the b_{2g}, b_{1g}, and a_{1g} orbitals (which are almost pure 3d in character), namely 8.55 to 10.36 eV. For the $4e_g$ orbital, however, where the 3d character is substantially reduced by 3d → π^* back-donation, the relaxation energy is much less, 3.55 eV.

The ΔSCF ionization potentials for the eclipsed and staggered conformers are compared in Figure 3. As expected, there are no large differences, confirming one's intuitive feeling that the D_{4h} and D_{4d} electronic structures are rather similar. As noted above, the doubly degenerate $3e_2$ orbital of the staggered conformer splits into the eclipsed orbitals $2b_{2g}$ and $3b_{1g}$, separated by 0.33 eV. A larger splitting occurs within the orbitals primarily of C–C σ bond character. Figure 3 shows that the D_{4d} orbital $4e_2$ splits into $1b_{1u}$ and $1b_{2g}$ components, separated by 0.77 eV. Finally, the small $D_{4h} - D_{4d}$ separation of about 1 kcal is not readily explained in terms of Figure 3. For example, the splittings of the D_{4d} $3e_2$ and $4e_2$ orbitals are relatively symmetric (i.e., one orbital is energetically favored, the other energetically disfavored) as the molecule proceeds from D_{4d} to D_{4h} symmetry.

It is also of considerable interest to compare Figure 3 with the qualitative textbook correlation diagram of Figure 1. The biggest difference is that four orbitals ignored in Figure 1 actually lie higher in energy than the $7a_{1g}$ orbital, which is clearly a π orbital. These four orbitals are primarily cyclobutadiene σ-like in character and disprove once again the literal notion (widely accepted 20 years ago) of σ–π separability.

Some features of Figure 1 are confirmed in Figure 3. For example, the ordering of CBD π orbitals as a_{1g}, a_{2u} (inadvertantly left out by Hall[10] in his version of Figure 1), e_u is that given by qualitative theory. Also the 3d ordering e_g, a_{1g}, $b_{1g} = b_{2g}$ is reproduced by the ab initio theory, although the $3b_{1g}$ and $2b_{2g}$ IP's actually differ by 0.33 eV, rather than being precisely equal. Furthermore, the placement of the $6e_u$ orbital (π-like) among the 3d-like orbitals is not unreasonable, since the corresponding bands in the photoelectron spectra of $(C_4H_4)Fe(CO)_3$ are quite close in energy.[29] The a priori theory places this π orbital in roughly the center of gravity of the d orbitals, while Hall's diagram places the $6e_u$ orbital somewhat lower. A more serious discrepancy between Figures 1 and 3 concerns the energy scale. In Figure 1 there is a large gap between the (b_{1g}, b_{2g}) pair of d orbitals and the $8a_{1g}$ orbital. The ΔSCF diagram, Figure 3, suggests that the four 3d-like orbitals fall in a much smaller energy range, only 1.44 eV, from which the two lower π orbitals are quite far removed.

Concluding Remarks

A reasonably comprehensive optimization of the geometry of $Ni(C_4H_4)_2$ has been carried out here with use of the restricted Hartree–Fock theory in conjunction with a relatively large basis set of one-electron functions. The resulting final wave functions allow us to make a detailed examination of the electronic structure of bis(cyclobutadiene)nickel in both its eclipsed and staggered conformations. We hope this theoretical research will provide a stimulus for the experimental determination of the properties of $Ni(C_4Ph_4)_2$, the first known cyclobutadiene sandwich compound.[5] A crystal structure would be particularly welcome. Furthermore, it is to be hoped that the unsubstituted parent compound will be synthesized in the near future.

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(29) M. B. Hall, I. H. Hillier, J. A. Connor, M. F. Guest, and D. R. Lloyd, *Mol. Phys.*, 30, 839 (1975).

Comparison of Equilibrium Constants in Gas and Liquid Phases

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Abstract: Available vaporization data have been used to compare gas-phase and liquid-phase equilibrium constants, K_l/K_g, for associative equilibria of hydrocarbons. For most equilibria involving *n*-paraffins K_l/K_g is close to unity over the entire range of temperature and molecular size for which vapor pressures of *n*-paraffins are available. However, when methane is a reactant, K_l/K_g values become considerably greater than unity. While this effect can be ascribed to the relatively low solubility of methane in *n*-paraffins, it also appears to be an example of a general phenomenon that arises when small molecules are involved in associative equilibria. Atoms and small molecules are inherently less stable in solution than are larger molecules. For equilibria involving hydrocarbons other than *n*-paraffins, the general finding is that $K_l/K_g \sim 1$ when solvation effects are not significant and when reactants and products do not have major structural differences. These results imply that bimolecular rate constants for sufficiently large reactant molecules will not be significantly different in the liquid and gas phase unless solvation or diffusion effects are present. For reactions involving small reactant species, such as methyl radicals or H atoms, rate constants *may* be significantly greater in solution than in the gas phase. These ideas have been applied to selected aspects of free-radical thermochemistry and kinetics.

In order to use empirical and estimated gas-phase thermokinetic data for interpretation of solution-phase chemistry, a reliable means for gas-to-liquid conversion of such data is needed. While relationships between gas- and liquid-phase rate and equilibrium constants have been of concern for many years, research directly focused on this area has been reported only intermittently, and much of this research has been based on a rather limited data base.

Both collision theory and transition-state theory have been used by a number of workers to estimate relative liquid-phase and gas-phase bimolecular rate constants, $k_{b,l}/k_{b,g}$. A general conclusion of that work is that in the absence of solvation effects bimolecular rate constants in the liquid phase, $k_{b,l}$, are greater than rate constants for corresponding reactions in the gas phase, $k_{b,g}$. Early theoretical work by Rabinowitch[1] indicated that liq-

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