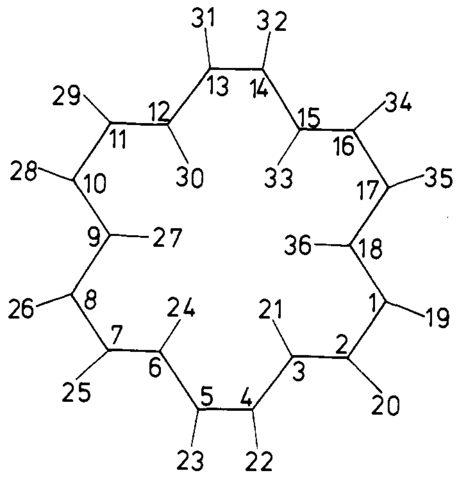

Figure 2. Structure and labeling of 18-annulene.

Table III. Geometries (Å and deg) and Total Energies (kcal/mol) of 18-Annulene

	SINDO1		MM[a]	ab initio[b]		exptl[c]
	D_{3h}	D_{6h}	D_3	D_{3h}	D_{6h}	$C_i(D_{6h})$
bond lengths						
C_1C_2	1.358	1.423	1.357	1.344	1.402	1.412
C_2C_3	1.495	1.418	1.465	1.455	1.389	1.377
C_3C_4	1.361	1.418	1.361	1.344	1.389	1.380
C_4C_5	1.502	1.423	1.465	1.455	1.402	1.429
bond angles						
$C_1C_2C_3$	125.5	126.7	126.0	124.1	124.2	123.6
$C_2C_3C_4$	130.6	133.4	123.2	128.3	128.4	127.8
$C_3C_4C_5$	125.1	126.7	123.2	124.3	124.2	122.9
$C_4C_5C_6$	125.1	126.7	126.0	124.3	124.2	124.0
energy						
SCF	21.1	59.4		139.5[e]	173.0[e]	
CI	11.7	8.7		100.2[e,f]	106.5[e,g]	
total	11.5[d]	0[d]		0[e,g]	24.9[e,g]	

[a] Reference 7. [b] Reference 8. [c] Reference 10. [d] With Davidson correction. [e] 6-31G* geometry, STO-3G basis. [f] With MP2. [g] With MP3.

is equal to C_3–C_4 in Figure 2. Later experimental studies support the delocalized form.[22] We have performed calculations for 18-annulene with SINDO1 similar to those for 14-annulene. The results are contained in Table III. The D_{3h} symmetry is much more stable on the SCF surface. The 60 configuration CI results in almost equal stability and the Davidson correction favors the D_{6h} structure. Again interpair type correlation is essential to lower the D_{6h} structure compared to the D_{3h} structure. Molecular mechanics results[7] favor a D_3 structure which is localized and slightly nonplanar. Ab initio calculations on the STO-3G level result always in a more stable D_{3h} structure even with perturbation correction of second and third order. However, 6-31G* calculations on the SCF level reduce the difference between the two structures to 16.4 kcal/mol compared to the 33.5 kcal/mol of the STO-3G calculation, both based on 6-31G* geometry. There is a chance that correlation will change the order of stability for the 18-annulene also on the ab initio level. Thiel[23] obtained similar results to ours in MNDOC calculations. With Davidson correction his D_{6h} structure is 1.1 kcal/mol below the D_{3h} structure.

A justification for the extensive use of CI in SINDO1 is given by comparison of calculated and experimental values of heat of formation. Oth et al.[22] deduce a value of 124 ± 6 kcal/mol from their measurement, which is close to the MM value[24] of 128.3 kcal/mol by Allinger. Dewar's MINDO/3 results in 129.1 kcal/mol for the D_{3h} structure and 154.8 kcal/mol for the D_{6h} structure. With the 60 configuration CI plus Davidson correction and with explicit calculation of zero-point energy we obtain a value of 147.5 kcal/mol for the D_{6h} structure and 158.9 kcal/mol for the D_{3h} structure. Since it is apparent from Table I that the absolute energy of the D_{6h} structure has not converged with a 60 × 60 CI, we expect from a larger CI a further lowering by more than 10 kcal/mol, which brings us closer to the experimental value. Without CI the SINDO1 heat of formation of 18-annulene would not be acceptable.

The classification of aromaticity according to the ring current criterion[13] yields results for 18-annulene similar to those for 14-annulene. The D_{6h} structure with an index of 1.72 would be termed aromatic, the D_{3h} structure with an index of 1.35 moderately aromatic close to nonaromatic.

V. Conclusion

It is gratifying to see that the geometries of the various symmetry types of structures of 14-annulene and 18-annulene are very close regardless of the theoretical method used. The stability of the structures depends on the level of accuracy of the calculation. Configuration interaction favors the delocalized form much more than the partially localized form on the semiempirical and the ab initio level. Interpair correlation and Davidson correction are essential to favor the stability of the delocalized structures. These structures can be called aromatic.

Acknowledgment. The calculations were performed on the CYBER 76 at Universität Hannover and the CRAY-1 at ZIB Berlin. We thank the Fonds der Chemischen Industrie for partial support of this work.

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A Triplet Ground State for the Planar Conformation of $(\mu\text{-NO})_2[Co(\eta^5\text{-}C_5H_5)]_2$?

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Abstract: Ab initio MO–SCF and multiconfiguration SCF calculations carried out on the d^9–d^9 complex $(\mu\text{-NO})_2[Co(\eta^5\text{-}C_5H_5)]_2$ indicate that the ground state of this molecule might be a triplet separated by 280 cm^{-1} from the associated covalent singlet. This conclusion is in agreement with the similarity of the metal–metal bond lengths observed for various d^8–d^8 and d^9–d^9 complexes. A careful reinvestigation of the magnetic susceptibility of the title compound is suggested.

The electronic structure of dibridged binuclear complexes of the type $(\eta^5\text{-}C_5H_5)_2M_2(NO)_{2-x}(CO)_x$ (x = 0, 1, 2; M = Fe, Co, Ni) has been the subject of continuing interest in the last 10 years.[1–8] This interest has been mainly focused on (a) the relation

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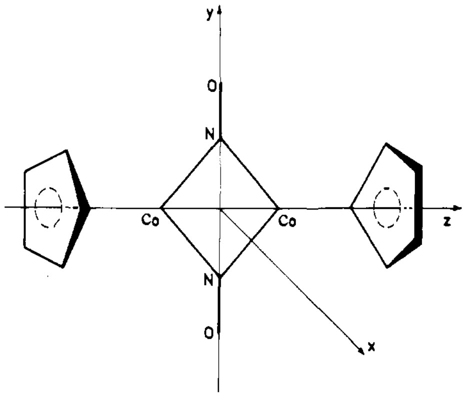

Figure 1. Representation of $(\mu\text{-NO})_2[\text{Co}(\eta^5\text{-C}_5\text{H}_5)]_2$ with the system of axes used in the calculations.

between the geometrical structure of the μ-L_2–M_2 core, bent or planar, and the d-electron count of the metal; (b) the nature of the metal–metal bond, formally double for the d^8–d^8 complexes and single for the d^9–d^9 ones, but susceptible to be delocalized over the M_2L_2 core through participation of the ligand π^* MOs;[3-8] and (c) the nature of the LUMO in the d^8–d^8 complexes, which is supposed to become the HOMO in the d^9–d^9 molecules.[1,2,5,6]

If some agreement has been reached for problem b on the presence of multicentered linkages delocalized over the M_2L_2 core,[3-8] the two other points remain controversial for the title compound. Actually, the $(\mu\text{-NO})_2$–Co_2 core of this d^9–d^9 complex has been shown to be planar in the solid state,[1] but an interpretation of the UV photoelectron spectra by means of discrete variational Xα calculations suggests a bent geometry in the vapor phase.[7] Concerning now point c, the problem raised by Bernal et al.[1] and by Pinhas and Hoffmann[2] about the geometrical implications of the nature of the HOMO remains open. According to Extended Hückel[2] and Fenske–Hall[6] calculations, this HOMO appears to be a combination of the d_{xz} Co orbitals (cf. Figure 1) with pure metal–metal antibonding character. The population of this MO was therefore expected to significantly increase the metal–metal distance for d^9–d^9 complexes, in contradiction with the similarity of the M–M bond lengths observed for various d^8–d^8 and d^9–d^9 molecules.

An alternative assignment of the HOMO of the title compound to one of the remaining NO π^* orbitals has then been considered and rejected for similar reasons:[2] no significant lengthening of the NO bond was observed on going from d^8–d^8 to d^9–d^9. The possibility for a high-spin ground state was clearly mentioned by Pinhas and Hoffmann,[2] but it was ruled out because of the reported diamagnetism of $(\mu\text{-NO})_2(\text{CoCp})_2$.[9] These pending problems prompted us to reinvestigate the electronic structure of this molecule by means of ab initio MO calculations,[10] using the experimental geometry reported by Bernal et al.[1] and slightly modelized in order to ensure a perfect C_{2h} symmetry[14] (Figure 1).

Table I. SCF and MCSF Energy (hartrees) of the Various Electronic Configurations Computed for $(\mu\text{-NO})_2[\text{Co}(\eta^5\text{-C}_5\text{H}_5)]_2$

configuration	nature	energy (hartrees)
$[2]^2[1]^2[3]^0$	singlet	-3399.2237
$[2]^2[3]^2[1]^0$	singlet	-3399.2418
$[2]^2[3]^1[1]^1$	triplet	-3399.4363
$[2]^2[1]^2[3]^0$ $-[2]^2[3]^2[1]^0$	singlet	-3399.4350

Results and Discussion

A first closed shell SCF calculation was carried out starting from the wave function of the parent compound $(\mu\text{-NO})_2(\text{Fe Cp})_2$,[8] a d^8–d^8 species, and assuming the two extra electrons to populate the

$$[d_{xz}(1) + d_{xz}(2)] \qquad (a_g) \qquad (1)$$

antibonding combination of metal orbitals. As mentioned earlier, this choice was consistent with the conclusions of all former theoretical studies.[2-4,6] It yielded a total energy of -3399.2237 hartrees (Table I).

At variance from MO (1), the metal–metal bonding combination of the d_{xz} orbitals can interact with the nitrosyl π_x^* combination of appropriate phase:

$$[\alpha(d_{xz}(1) - d_{xz}(2)) + \beta\pi_x^*(\text{NO})] \qquad (b_u) \qquad (2)$$

$$\text{with } \beta > \alpha$$

This doubly occupied MO results in one of the two electron/four center interactions ensuring the stabilization of any complex of the type $\text{Cp}_2\text{M}_2(\text{NO})_{2-x}(\text{CO})_x$.[17] Due to the strong π-acceptor character of the nitrosyl ligand, the major weight in this combination comes from the NO π^* orbitals, in agreement with the recent results of Schugart and Fenske.[6] The counterpart of this MO is a low-lying combination of b_u symmetry with metal–metal bonding and metal–ligand antibonding character, and with major weight on the metal:

$$[\beta(d_{xz}(1) - d_{xz}(2)) - \alpha\pi_x^*(\text{NO})] \qquad (b_u) \qquad (3)$$

This combination appeared as the LUMO in the calculation and the corresponding electronic configuration can be labeled as $[1]^2[2]^2[3]^0$.

A second closed shell SCF calculation was then carried out assuming the electronic configuration $[2]^2[3]^2[1]^0$. Rather surprisingly, a lower value was found for the total energy, with an

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(10) All calculations have been carried out with the ASTERIX system of programs adapted to the IBM 3081 computer.[11] The Gaussian basis set was triple-ζ for the metal d shells and double-ζ for the valence orbitals of first-row atoms. The basis set for cobalt was taken from the (13,7,5) set of Hyla-Kryspin et al.,[12] incremented with one p function of exponent 0.15 and one d function of exponent 0.10, and then contracted to [5,3,3]. Basis sets (9,5) and (4) were used for first-row atoms and hydrogen respectively and contracted to split valence.[13]

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(14) The selection of the C_{2h} point group (with staggered C_5H_5 rings) with respect to the C_{2v} point group (with eclipsed Cp rings) is not an innocent choice, even though the rotation barrier of the Cp ring is expected to be negligible.[2] Calculations on the related molecule $\mu(\text{NO})_2[\text{FeCp}]_2$[15] have shown that the distribution of the four nitrosyl π^* orbitals (two occupied and two unoccupied) into four different irreducible representations occurring under the C_{2v} symmetry constraints resulted in Hartree–Fock instability of the singlet type.[16] The choice of the C_{2h} point group releases the symmetry constraints affecting the NO π^* orbitals and yields a singlet stable and more realistic description of the electronic structure of the molecule at the SCF level.[15]

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(16) Concerning Hartree–Fock instability, see, for example: Čížek J., Paldus J. *J. Chem. Phys.* **1967**, *47*, 3976. Böhm, M. C. *Chem. Phys. Lett.*, **1981**, *81*, 284; *Theor. Chim. Acta* **1981**, *60*, 233. Bēnard, M. *J. Chem. Phys.* **1979**, *71*, 2546. Wiest, R.; Bēnard, M. *Theor. Chim. Acta* **1984**, *66*, 65. Davidson, E. R.; Borden, W. T. *J. Phys. Chem.* **1983**, *87*, 4783.

(17) The other delocalized interaction occurs in the M_2L_2 plane and involves a metal–metal antibonding combination of the type $[\mu(d_{yz}(1) + d_{yz}(2)) + \nu\pi_z^*(\text{NO})]$ (b_g).

energy gap of 11 kcal/mol only between the two configurations (Table I). This result was a first clue to the possibility of a nondiamagnetic ground state for $(\mu\text{-NO})_2(\text{CoCp})_2$. Further evidence had to be gained from direct calculations on the triplet configuration $[2]^2[1]^1[3]^1$ and on the associated covalent singlet state described in the first approximation by the two-configuration expansion $[2]^2[1]^2[3]^0 - [2]^2[3]^2[1]^0$. The calculation on the triplet state was carried out by means of a one-configuration open-shell SCF calculation and the singlet state was independently optimized through a MCSCF treatment taking as reference states the two closed-shell configurations $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$. This formalism allows a determination of the singlet–triplet splitting accounting for both the exchange term $2K_{ab}$ and the superexchange contribution.[18] Moreover, the set of MOs is allowed to relax independently for the singlet and the triplet states.

Both the triplet and the two-configuration singlet states were found to be lower in energy by about 120 kcal/mol than the individual $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$ configurations (Table I). The triplet state appears to be lower in energy than the two-configuration singlet by 0.0013 hartree (280 cm^{-1}). This relative ordering is in agreement with the almost opposite weights (respectively 0.7095 and –0.7047) of the $[2]^2[1]^2[3]^0$ and $[2]^2[3]^2[1]^0$ configurations obtained in the MCSCF expansion.[18]

It must be kept in mind, however, that the reported calculations were carried out on an isolated molecule assuming a perfectly planar and undistorted geometry. The narrow singlet–triplet energy gap can be affected by the crystal packing forces and more specifically by the slight deviations from planarity observed in the crystal (0.004 Å).[1] Even if the high-spin character of the title compound is not definitely established by the present work, it appears that the singlet–triplet separation will remain weak. This means that the two extra electrons of the d^9–d^9 complexes have almost pure metal character, but they are globally nonbonding with respect to the metal atoms. This result is in perfect agreement with the observed stability of the metal–metal distances in d^8–d^8 and d^9–d^9 complexes, but it clearly questions the reported diamagnetism of $(\mu\text{-NO})_2[\text{CoCp}]_2$. A careful survey of the literature indicates that the only report on the magnetic behavior of $(\mu\text{-NO})_2[\text{CoCp}]_2$ is due to Brunner.[9] The diamagnetism was deduced only from the proton NMR spectrum.[9] No report of the temperature dependence of the magnetic susceptibility was provided, and it therefore seems that a ferromagnetic or antiferromagnetic interaction cannot be ruled out. In view of the present theoretical results, we therefore suggest a careful reinvestigation of the magnetic susceptibility of $(\mu\text{-NO})_2[\text{CoCp}]_2$.

Acknowledgment. All calculations have been carried out on the IBM 3081 of the Centre de Calcul de Strasbourg-Cronenbourg. We thank the staff for cooperation.

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(18) The singlet–triplet splitting can be expressed as $E_S - E_T = 2K_{ab} - [(\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab})]$, where J_{aa}, J_{ab}, and K_{ab}, computed on the triplet MO basis, are positive coulomb and exchange integrals, ϵ_1 and ϵ_2, representing the orbital energies of the open shells. The second term is the superexchange contribution, which is accounted for by the separate MCSCF optimization of the singlet state. This contribution vanishes for the degenerate case corresponding to equal values for ϵ_1 and ϵ_2 and to opposite expansion coefficients in the MCSCF treatment, thus yielding a positive value for $E_S - E_T$.[19]

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Electrically Controlled Release of $Fe(CN)_6^{4-}$ from Polypyrrole

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Abstract: The anodic polymerization of pyrrole onto glassy carbon in the presence of aqueous $K_4Fe(CN)_6$ gave a polypyrrole which incorporated $Fe(CN)_6^{3-}$ (PP/FCN). The polymerization process for PP/X$^-$ (X = ClO_4, Cl, BF_4, PF_6) and PP/FCN was studied using chronoamperometry and showed nucleation and growth kinetics. The concentration of electrolyte and pyrrole governed the nucleation and growth rates. It was shown that stirring inhibits both nucleation and growth, suggesting the involvement of soluble species in film formation. Higher electrolyte concentrations gave films with larger electrical capacities as evaluated by cyclic voltammetry. The extent of incorporation of $Fe(CN)_6^{3-}$ depended on the relative concentration of $Fe(CN)_6^{4-}$ and ClO_4^- in the solution from which the film was grown. In these PP/FCN films, the FCN does not readily exchange with other ions in aqueous solution and can only be flushed out of a film (formed with Q = 2 mC cm^{-2}) into aqueous 0.1 M NaCl solution at potentials more negative than –0.4 V vs. SCE. A thinner film which had been formed with Q = 0.22 mC cm^{-2} gave release into 0.1 M NaCl only at –0.6 V. It is shown that little FCN is cathodically released into aqueous CsCl or tetraethylammonium chloride solutions. X-ray photoelectron spectroscopy indicates instead that Cs$^+$ is bound into the reduced PP/FCN film. It was demonstrated that repetitive 5-s pulses to –0.4 V from open circuit gave controlled release of FCN into a small volume of solution. PP/FCN films changed, giving smaller release amounts, when they were allowed to dry.

The considerable current interest in conducting polymers has led to a number of apparent applications and to the beginnings of understanding of the structure and properties of these materials.[1] Our interest is in the electrochemical properties of conducting polymers and their use for the controlled release of chemicals, especially drugs.[2,3] The basic concept of this application is to bind the drug into a polymer film on an electrode and release the drug as needed by passing a small current through the polymer.[4] A simple approach to this problem is to bind ionic drugs into an ionic redox polymer coated on an electrode and then force the drug ion out by neutralizing the charge on the polymer. Specifically, one should be able to bind anions into a cationic polymer like polypyrrole and release the anion by reducing the cationic backbone. Because the polymer is conductive, it should allow binding and release throughout thick films, in turn allowing relatively large amounts of ions to be released. The detailed structure of polypyrrole (PP) is not well established, and it is not

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(1) For an extensive current review see: *Handbook of Conducting Polymers*; Vol. I, II; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986.

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