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ELECTRON DIFFRACTION STUDY IN THE VAPOUR PHASE OF THE MOLECULAR STRUCTURE OF DICYCLOPENTADIENYLNICKEL

I. A. RONOVA, D. A. BOCHVAR, A. L. CHISTJAKOV, YU. T. STRUCHKOV AND N. V. ALEKSEEV
Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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SUMMARY

The molecular structure of nickelocene, $(C_5H_5)_2Ni$, has been studied by electron diffraction in the vapour phase. The molecule has eclipsed configuration with Ni–C 2.160, C–C 1.41 and C–H 1.10 Å. C–H bonds are bent out of the planes of the cyclopentadienyl rings towards the metal atom by 5°. This effect, which is general for dicyclopentadienyl sandwich compounds, is interpreted in terms of the new electron gas model as being a result of the repulsion between the electron clouds of the C–H bonds and the π-electron density of the cyclopentadienyl ring.

INTRODUCTION

The crystal structure of dicyclopentadienylnickel (nickelocene) has not been investigated in any detail by X-ray diffraction. However, it was found[1,2] that this compound (as with others in the series of dicyclopentadienyl derivatives of transition metals) is isostructural with ferrocene. The unit cell parameters of nickelocene were determined by Schneider and Fischer[3], and for all ferrocene-like compounds[4] only the *b* and *c* parameters were found to vary on going from one metal to another. Because the five-fold axes of molecules coincide approximately with the direction of the *bc*-diagonals of unit cells, and assuming an invariance of the carbon–carbon bond length in all isostructural compounds, the metal–carbon and metal–cyclopentadienyl ring centre distances may be estimated. The Ni–C bond distance thus found is *ca.* 2.2 Å. Evidently, this value is only approximate. To establish the molecular geometry with reasonable precision we undertook the present structural study of nickelocene by electron differaction in the vapour phase.

EXPERIMENTAL

A sample of nickelocene was purified by repeated sublimation in an argon atmosphere. The evaporator ampoule was filled with nickelocene in a dry argon box to avoid contact with atmospheric oxygen. The evaporation temperature was *ca.* 90°.

The electron diffraction patterns were recorded in the EG-100a electronograph with the r^3-sector. The nozzle-to-plate distance was *ca.* 400 mm throughout all experiments and accelerating potentials of 40 and 80 kV were used. After densitometric processing, 20 curves taken at 40 kV and 15 curves taken at 80 kV were selected for further work. The initial correction and processing of experimental data were made as described previously[5-7]. The resulting molecular intensity curve covers the interval $s = 1.9\text{–}21.5$ Å^{-1} (Fig. 1).

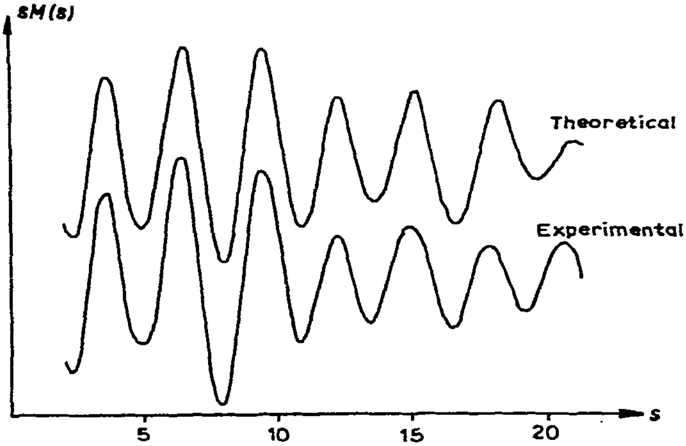

Fig. 1. Theoretical and experimental molecular intensity curves. The theoretical curve is calculated for the eclipsed configuration.

First, the extrapolation of the experimental molecular intensity curve, $sM(s)$, into the region of small s-values was fulfilled by Fourier inversion of the structural part of the radial distribution (RD) curve, $f(r)$, taking into account the non-negativity of the experimental RD curve in this region. Later, the missing part of the experimental $sM(s)$ curve, $s = 0\text{–}1.9$ Å^{-1} was substituted by a fragment of the theoretical $sM(s)$ curve which was based on the structural data found in this stage of the investigation. At this point non-nuclear scattering was also taken into account. Molecular contribution to the electron scattering intensity including form-factors was calculated in the first Born approximation according to

$$sM(s) = \frac{1}{\sum\limits_{i=1}^{k} m_i [f_i^2(s) + S_i(s)/s^4]} \cdot \sum_{p=1}^{N} \frac{n_p f_q(s) f_t(s)}{r_p} \cdot \cos s\delta_p \exp[-l_p^2 s^2/2] \cdot \sin s[r_p + k_p s^2]$$

Here $f(s)$ is calculated using Hartree–Fock[8] or Thomas–Fermi–Dirac[9] potentials. The function of non-coherent electron scattering, $S(s)$, is taken from Tietz's equation[10].

Structure analysis

The experimental RD curve was interpreted with the usual assumption of cyclopentadienyl ring geometry (planar regular pentagon). In this case, for full determination of the molecular geometry of nickelocene it is necessary to obtain independent parameters, $r(C_1\text{–}C_2)$, $r(\text{C–H})$, $r(\text{Ni–C})$, $r(\text{Ni...H})$, and the relative orientation of cyclopentadienyl rings, which were assumed to be parallel (eclipsed or staggered model, see Fig. 2).

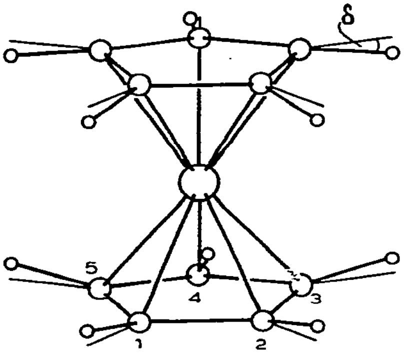

Fig. 2. The general geometry of the nickelocene molecule.

The experimental RD curve has four peaks (Fig. 3). The first at 1.41 Å corresponds to the C–C bond lengths in the cyclopentadienyl rings. The shoulder of this peak at 1.10 Å corresponds to the C–H bond distance. The values found are in good agreement with analogous distances in the structures of the dicyclopentadienyl derivatives of transition metals previously studied by electron scattering[11-14].

The next peak at 2.19 Å is composite, the main contribution is from the Ni–C distance but it also contains the component corresponding to the non-bonded $C_1...C_3$ distance in the cyclopentadienyl ring. The refinement of these values by least-squares in a version of stage-by-stage parameter refining[15] shows that all Ni–C distances are equivalent and equal to 2.160 Å.

The third peak at 2.851 Å is individual and corresponds to the Ni...H distance. The last complex of unresolved peaks represents distances between carbon atoms in different ligand rings. The comparison of the experimental RD curve in this region with theoretical curves calculated for staggered (curve a) and eclipsed (curve b) models shows that the model with eclipsed arrangement of rings is preferable. The validity of this conclusion on structure is confirmed by the good agreement between the experi-

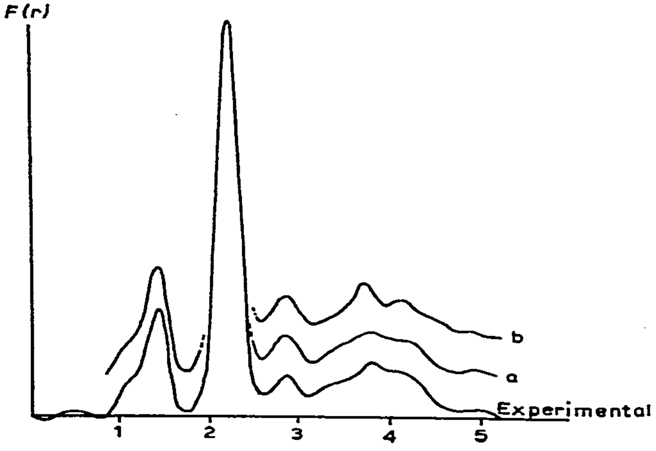

Fig. 3. Experimental and theoretical RD curves: (a) eclipsed; (b) staggered model.

TABLE 1

GEOMETRICAL PARAMETERS OF NICKELOCENE AND OTHER SANDWICH MOLECULES STUDIED BY ELECTRON DIFFRACTION IN THE VAPOUR PHASE

Molecule	C(1)–C(2) (Å)	C–H (Å)	M–C (Å)	M...H (Å)	δ (°)	Configuration	Ref.
$(C_5H_5)_2Mn$	1.429±0.005	1.133±0.023	2.383±0.009	2.805±0.026	6.5±4.1	Staggered	14
$(C_5H_5)_2Fe$	1.429±0.003	1.116±0.013	2.056±0.005	3.044±0.054	4.6±2.7	Eclipsed	11
$(C_5H_5)_2Ni$	1.41±0.01	1.10±0.02	2.160±0.005	2.851±0.02	5±2	Eclipsed	
$(C_5H_5)_2Ru$	1.438±0.002	1.130±0.006	2.196±0.003	—	—	Eclipsed	20
$(C_5H_5)_2Pb$	1.430±0.010	1.105±0.018	2.778±0.016	3.421±0.040	—	Not determined	13
$(C_5H_5)_2Sn$	1.431±0.009	1.142±0.024	2.706±0.024	—	—	Not determined	13
$(C_5H_5)_2Be$	1.424±0.002	1.070±0.005	1.915±0.005 2.320±0.010	2.720±0.020 3.020±0.030	—	Staggered	12

mental curve and the best of the theoretical $sM(s)$ curves (Fig. 1). The nickelocene molecular parameters obtained as described above are given in Table 1.

DISCUSSION

The RD curve shows that all Ni–C distances in the nickelocene molecule are equal to 2.160 Å. This value is in reasonably good agreement with the distance, 2.2 Å, estimated on the basis of isomorphism with ferrocene. Pauson in his review cites an unpublished electronographic study of nickelocene in which a value of 2.18 Å is given for the Ni–C distance[16].

The RD curve shows that the eclipsed orientation of the cyclopentadienyl rings is more probable. Dicyclopentadienyl derivatives of transition metals in the crystalline state have either D_{5d} symmetry, *i.e.*, the ferrocene-like staggered conformation, or D_{5h} symmetry as in the case of ruthenocene, *i.e.*, an eclipsed configuration.

However, according to the electron diffraction study in the vapour phase (see Table 1) most of these compounds have a predominantly eclipsed configuration with a low barrier of internal rotation (*e.g.*, 0.9±0.3 kcal/mole for ferrocene[21]). Therefore, it may be assumed that the different configuration in the solid state is due probably to packing effects, *i.e.*, to crystal field forces.

The Ni...H distance found for nickelocene is 2.851 Å. Thus, it is 0.075 Å less than the value calculated under the assumption of an ideal C–H bond direction, *i.e.*, in the cyclopentadienyl ring plane and along bisectors of the C–C–C bond angles. The observed shortening would correspond to a bending of the C–H bonds of $\delta \approx 5.0°$ out of the ring plane towards the metal atom.

A similar effect was observed in the electron diffraction study[11] of ferrocene vapour; in this case $\delta = 4.6°$ and it was assumed by the authors that the ligands had been distorted by the metal atom field. If this assumption is valid, the distortion, δ, must diminish with the growing metal-to-ring distance. In the dicyclopentadienylmanganese molecule[14], the bending of the C–H bonds is $\delta = 6.5°$, *i.e.*, larger than in ferrocene, but the metal-to-ring distance is also much longer. This discrepancy compelled the authors[14] to discard their former interpretation[11] and they concluded that the observed shortening of the metal-to-hydrogen distance is due to shrinkage effects, *i.e.*, the larger the amplitude of out-of-plane vibrations of hydrogen atoms the shorter is the experimental M...H distance compared with the equilibrium value. However, this latter interpretation is not altogether satisfactory. The effective displacement of hydrogen atoms resulting from out-of-plane vibrations must have a fixed direction and must not depend on the number of cyclopentadienyl rings in the molecule provided that the inter-ring H...H distances are greater than the doubled Van-der-Waals radius. However, it is difficult to explain the fact that in the monocyclopentadienylindium molecule, hydrogen atoms are also displaced out of the ring plane but in the opposite direction, *i.e.*, away from the metal atom[17].

In this communication we wish to emphasize that the values of the experimentally found out-of-plane C–H bond bending are in a good agreement with the electron density distribution calculated for the molecules under discussion on the basis of the new electron gas model. This model was proposed[18] for calculation of conjugated systems of transition metal dicyclopentadienides. The model is represented as a system described by the Schrödinger equation with a constant potential and with a region of determination on the lateral surface of a cylinder. It should be stressed that not a model of the molecule itself is constructed but a model of the phenomenon of conjugation in a molecule possessing a quantum nature. Thus the model mentioned may be considered as a specific composition of two one-dimensional models (a conjugation between rings is imposed on the conjugation in rings).

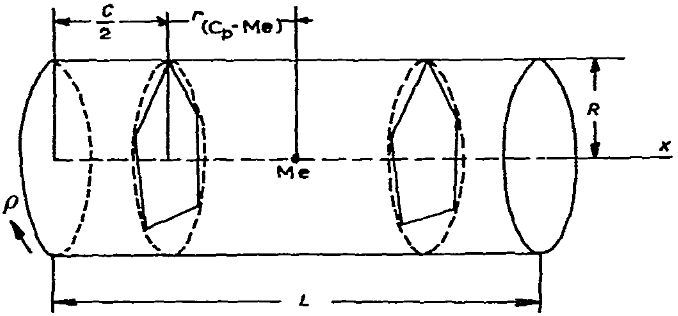

Fig. 4. Coordinate system on the cylinder surface that represents a region of determination for the Schrödinger operator in the electron gas model of sandwich compounds.

The cylinder chosen passes through the carbon atoms of the cyclopentadienyl rings (Fig. 4) and its parameters correspond to experimental data. The radius, R, is equal to the ring radius, the height is $L=2r_{(M-Cp)}+C$, where $r_{(M-Cp)}$ is the metal-to-cyclopentadienyl plane distance and C is the cyclopentadienyl ring Van der Waals thickness, 3.40 Å[19]. Cylinder coordinates, x, ρ, are determined according to Fig. 4 ($0 \leqslant x \leqslant L$, $0 \leqslant \rho \leqslant 2\pi R$).

Mathematically the model is formulated as a following boundary problem (here m_0 is the electron mass):

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial \rho^2}+\frac{2m_0}{\hbar^2}E\right)\psi(x,\rho)=0$$

$$\psi(0,\rho)=\psi(L,\rho)=0,\ \psi(x,2\pi R)=\psi(x,0)$$

The solutions are

$$E_{lq} = \frac{\hbar^2}{2m_0}\left[\frac{l^2}{R^2} + \frac{\pi^2}{L^2} q^2\right],$$

$$\psi_{lq}(x,\rho) = (\pi R L)^{-\frac{1}{2}} \exp\left[\left(i\frac{l\rho}{R}\right)\sin\left(\frac{\pi q x}{L}\right)\right],$$

$l=0, \pm 1, \ldots; q=1, 2, \ldots$

In this calculation, π-electrons of the rings and the metal valence electrons only are included.

The electron density distribution, $F(x)$, along the x-axis found from the many-electron wave function by averaging over all electrons (with the exception of one electron) and also by averaging over the ρ-coordinate is given in Fig. 5. For ease of comparison all the L-parameters are reduced to the length π by choosing a new variable, $x' = x\pi/L$. The ring position in this Figure is denoted by the value, $\gamma = C\pi/2L$.

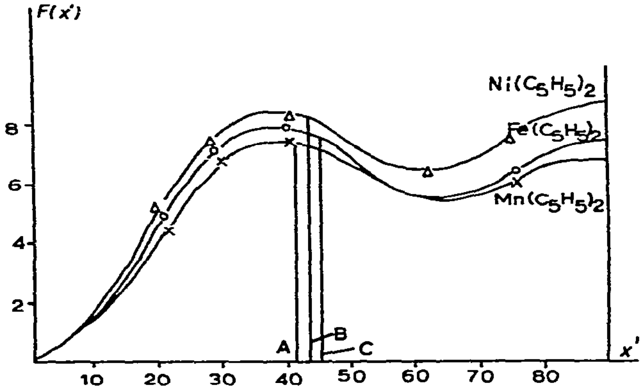

Fig. 5. The electron density distribution along the symmetry axis in Cp_2M molecules. A, B, C—positions of the cyclopentadienyl ring in Cp_2Mn, Cp_2Ni and Cp_2Fe, respectively.

For the monocyclopentadienylindium molecule, the cylinder considered has height, $L = C/2 + r_{(\mathrm{In-Cp})} + \lambda$, the λ-value being varied between 1.5 and 3.0 Å*. The electron density of the C_5H_5In molecule along the symmetry axis is given in Fig. 6.

Figures 5 and 6 show that in Fe-, Ni- and Mn-dicyclopentadienyls the electron density maxima in the neighbourhood of the cyclopentadienyl ring are displaced outwards from the metal atom. On the contrary, in the C_5H_5In molecule this displacement takes place in the opposite direction, *i.e.*, towards the metal atom, for any λ-value in the interval indicated. It is natural to suppose that the direction of the C–H bonds deflection is determined by the interaction between the electron clouds of these bonds and the π-electron density of the conjugated system, so that the local characteristics of the electron density distribution, $F(x)$, in the neighbourhood of the cyclopentadienyl ring must be of governing importance.

The C–H bond electron cloud is repelled by the electron density "hunch" in the neighbourhood of the ring and if this "hunch" is located behind the ring the C–H

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* The value 1.5 Å is equal within some hundredths of Å to the metallic and covalent (tetrahedral) radius of indium.

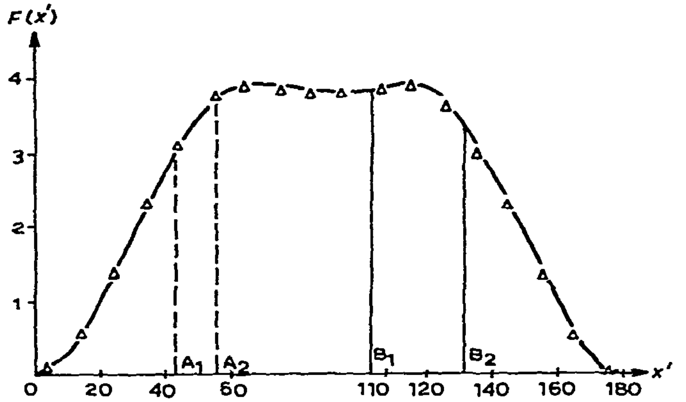

Fig. 6. The electron density distribution along the symmetry axis in the CpIn molecule. A_1 and A_2—cyclopentadienyl ring positions for $\lambda = 3.0$ and 1.5 Å, respectively; B_1 and B_2—corresponding In atom positions.

bond must be deflected to the metal atom, as for instance in Cp_2Fe, Cp_2Mn and Cp_2Ni. On the contrary, if the ring electron density maximum is located between the metal atom and the ring, this deflection must have the opposite direction as, for instance, in C_5H_5In.

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