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Electronic structure of bis-arene-chromium complexes

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Abstract

Dibenzenechromium derivatives of the type $(C_6H_5R^1)Cr(C_6H_5R^2)$ have been studied by He-I photoelectron spectroscopy. Substituent parameters have been found which allow the first and second ionization potentials of the bis-arene-chromium complexes to be determined using a very precise additive scheme. It has been shown that the change in the energy of the highest occupied MOs of the molecules is determined by the electrostatic field of ligands. The molecular electrostatic potentials of a number of species $(C_6H_5R^1)(C_6H_5R^2)$ have been calculated and the equation relating IP to $\varphi(R)$ has been found. A scheme for constructing the energy level diagram for dibenzenechromium and its derivatives is suggested.

The electronic structure of dibenzenechromium (I) has long been the subject of both quantum chemical calculations [1–4] and experimental investigations by photoelectron spectroscopy (PES) [1,3,5] and by electron transmission spectroscopy (ETS) [6]. Nevertheless, this problem continues to arouse interest.

This paper presents the results of investigation by the method of He-I PES of a number of non-symmetrically disubstituted dibenzenechromium compounds of the type $(C_6H_5R^1)Cr(C_6H_5R^2)$, where R^1 = CN and R^2 = CH_3 (II), OCH_3 (III), H (IV), Cl (V), F (VI), CF_3 (VII) and CN (VIII), as well as the results of calculations for ligand group orbitals by the MNDO method [7].

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Results and discussion

The vertical ionization potentials (IPs) of dibenzenechromium (I) and compounds II–VIII are listed in Table 1. The PE spectrum of VII, typical for the whole series of the bis-arene-chromium complexes, is shown in Fig. 1.

Analysis of the PE spectra of I–VIII has allowed us to establish the following. The first three bands are well resolved and have similar shapes for the whole series of compounds. The IP_1, IP_2, IP_3 and IP_4 are shifted towards higher values with increasing electron-withdrawing ability of the substituents in the arene ligands. The difference between the first and the second IP ($\Delta\ IP_{1,2}$) is 1 eV, which is retained

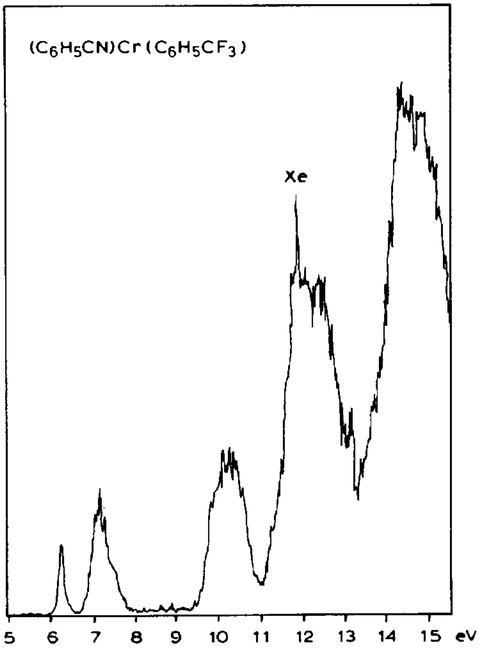

Fig. 1. He-I photoelectron spectrum of $(C_6H_5CN)Cr(C_6H_5CF_3)$.

Table 1

Ionization potentials (IP) of bis-arene-chromium complexes of the type $(C_6H_5R^1)Cr(C_6H_5R^2)$

	R^1,R^2	Ion state and IPs (eV)				Centre of mass of 3rd band (eV)
		$^2A_{1g}$ (IP_1)	$^2E_{2g}$ (IP_2)	$^2E_{1u}$ (IP_3)	$^2E_{1g}$ (IP_4)	
I	H,H	5.40	6.40	unresolved		9.6
II	CN,CH_3	5.73	6.70	9.61	9.97	9.81
III	CN,OCH_3	5.75	6.75	9.10	10.00	–
IV	CN,H	5.85	6.89	9.93	10.41	10.13
V	CN,Cl	6.09	7.09	9.70	10.5	10.05
VI	CN,F	6.14	7.09	9.93	10.49	10.20
VII	CN,CF_3	6.21	7.21	unresolved		10.39
VIII	CN,CN	6.41	7.41	10.14	10.54	–

throughout the whole series with a high degree of precision. It was shown in ref. 5 that the value of Δ $IP_{1,2}$ for certain symmetrically substituted chromium complexes ($R^1 = R^2 = F$, OC_6H_5, etc.) can decrease to 0.8–0.9 eV.

Comparison of our experimental data with those in ref. 5 has shown that the dependences of IP_1 and IP_2 of both symmetric and non-symmetric bis-arene-chromium complexes with 1–4 substituents of $(C_6H_4R^1R^2)Cr(C_6H_4R^3R^4)$ are described by:

$$IP_1 = 5.40 + \sum_{i=1}^{N} \Delta(R^i) \tag{1}$$

$$IP_2 = 6.40 + \sum_{i=1}^{N} \Delta(R^i) \tag{2}$$

where N is the number of R^i substituents, $\Delta(R^i)$ is the shift of values, typical for each one of them. From the data in Table 1 and ref. 5, we obtain: $\Delta(CH_3) = -0.05$, $\Delta(OCH_3) = -0.1$, $\Delta(Cl) = 0.20$, $\Delta(F) = 0.25$, $\Delta(CF_3) = 0.33$, $\Delta(CN) = 0.50$ eV.

The correlation coefficient for the dependence between the IPs calculated from formulae 1 and 2 and those from experimental data is 0.995. The standard deviation is 0.05 eV for IP_1 and 0.11 eV for IP_2. The regularity established points to the additive character of the influence of substituents on the first and second ionization potentials. It allows us to estimate, with high precision, the IPs of the unstudied compounds of this series.

The same linear dependence was found between the IPs of the complexes * and the sums of the substituent $\sigma_m{}^0$ constants [8] in accordance with eq. 3, the correlation coefficient being equal to 0.990.

$$IP_1 = 0.79(\pm 0.03)\sum\sigma_m^0 + 5.34(\pm 0.03) \tag{3}$$

High correlation coefficients were also obtained when σ_m and σ_m^+ ($r = 0.988$ and 0.979, respectively) were used. Such a correlation provides evidence for the predominantly inductive mechanism for transmission of substituent electronic effects to the chromium atom. The same conclusion was made earlier, on the basis of data on the anodic oxidation of bis-arene-chromium complexes [9].

Electronic structure of dibenzenechromium

At the present time, the order of molecular orbitals (MO) responsible for the appearance of the first three bands in the PE spectrum of dibenzenechromium has been reliably established [1,2,5]. The first narrow band is attributed to the removal of an electron from the a_{1g}-type (D_{6h} symmetry) MO localized for 92–95% on the $3d_{z^2}$-atomic orbital (AO) of chromium. The second IP corresponds to ionization of the e_{2g}-MO formed for 50–60% by $d_{x^2-y^2}$ and d_{xy}-Cr AO. The third hand is assigned to ionization of the ligand π-MOs of the e_{1u} and e_{1g}-symmetries.

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* We have used the IP values for the $Arene_2Cr$ complexes investigated in this paper (I–VIII) (Table 1) as well as in ref. 5 (Arene = $CH_3C_6H_5$, FC_6H_5, ClC_6H_5, m-$(CF_3)_2C_6H_4$, p-$F_2C_6H_4$, p-$FC_6H_4CF_3$, p-$CH_3C_6H_4Cl$, 1,3,5-$(CH_3)_3C_6H_3$).

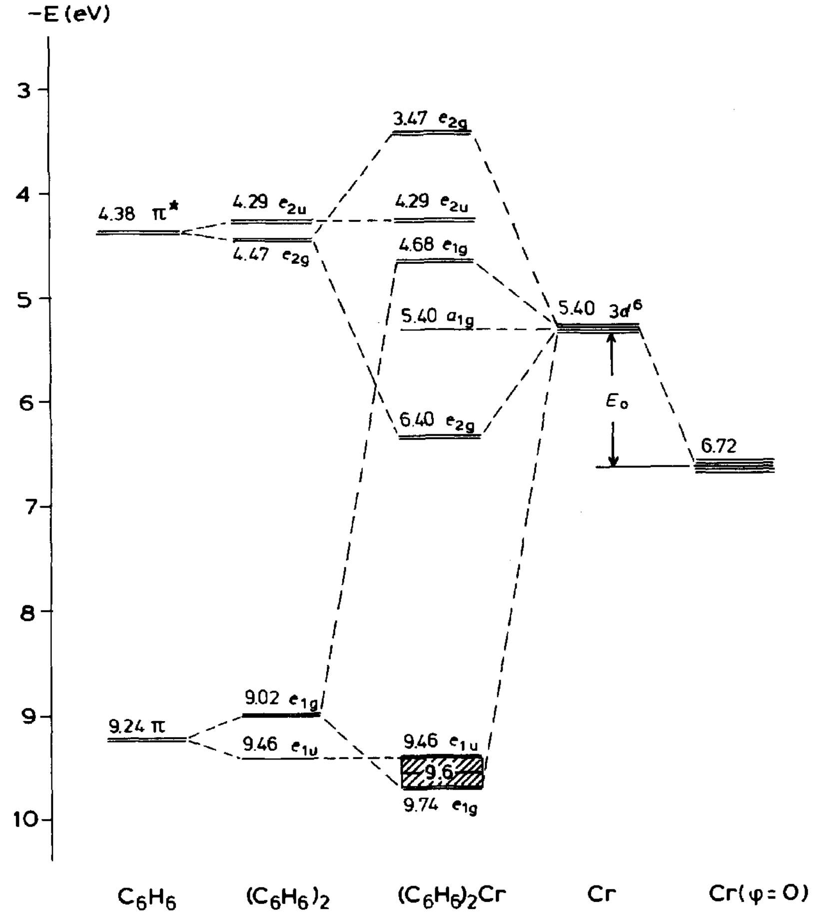

Fig. 2. Energy level diagram for dibenzenechromium. See discussion in the text.

The energy level scheme of the dibenzenechromium orbitals can be constructed by using the fragment approach, the interacting fragments being the ligand dimer $(C_6H_6)_2$ and the chromium atom (Fig. 2).

The electronic structure of $(C_6H_6)_2$ was calculated by the MNDO method. The interatomic C–C and C–H distances were chosen as 1.40 and 1.10 Å, respectively. The benzene rings were located in parallel planes at a distance of 3.22 Å to each other, which corresponds to the interplanar distance in dibenzenechromium [10].The calculations have shown that there is a considerable interaction between the π-MOs of the benzene rings. Thus, according to the calculations, the energy separation between the upper (e_{1g}) and the second (e_{1u}) occupied π-MOs of the $(C_6H_6)_2$ system is 0.44 eV, while the same gap between the lower (e_{2g}) and the second (e_{2u}) vacant π-MOs is 0.18 eV. These $(C_6H_6)_2$ dimer MOs are apparently the bonding and antibonding combinations of the benzene MOs.

In first-order perturbation theory the destabilizing value of the dimer π-orbitals, the e_{1g} MOs, relative to the benzene parent π-MOs equals the stabilizing value of the e_{1u} MOs. Hence, the absolute values of the orbital energy for the occupied e_{1g} and e_{1u} $(C_6H_6)_2$ MOs may be taken as being $9.24–0.22 = 9.02$ eV and $9.24 + 0.22 = 9.46$ eV ($9.24 - IP_1$ of benzene).

In order to determine the energies of the vacant e_{2g}- and e_{2u}-levels of $(C_6H_6)_2$, it is necessary to know the π^*-MO energy of benzene. According to UV spectroscopic data [11], the energy of the first $\pi \rightarrow \pi^*$ transition in benzene is 4.86 eV, whereas for $(C_6H_6)_2$ the energy of the e_{2g}-level is $9.24 - 4.86 + 0.09 = 4.47$ eV, and that of the e_{2u}-level is $9.24 - 4.86 - 0.09 = 4.29$ eV. The basis of such an estimation of vacant energy levels of $(C_6H_6)_2$ is the approximation used also in crystal field theory [12] when the experimentally observed optical transition energies are equal to the energy level separation between the d-levels of the metal atom. It should be noted that the sequence of the $(C_6H_6)_2$ π-MOs and the values of the energetic splitting between them were determined from calculated data, whereas the absolute values for the energy levels were obtained from PE and UV spectroscopic data. The term "level" underlines the distinction of the values in question from the MOs of the one-electron Hartry–Fock approximation.

The energy position of the degenerated $3d^6$ AOs of the Cr atom located in the symmetry centre of $(C_6H_6)_2$ depends on the electrostatic field value. The $3d$(Cr) level shift due to the ligand field is designated by E_0. The physical nature and estimation of E_0 for dibenzenechromium and other complexes are discussed below.

Let us consider the interaction of two fragments: $(C_6H_6)_2$ and the Cr atom. Interaction occurs between the (C_6H_6) π-MOs (e_{1g} and e_{2g}) and the Cr $3d^6$-AOs which are suitable in symmetry. The energy levels of the complex $(C_6H_6)_2Cr$ are shown in the middle part of the diagram in Fig. 2. The dimer π-orbitals of e_{1u} and e_{2u} type have no symmetry partner among the Cr $3d^6$ AOs. Therefore, they retain their energy in the complex. For the same reason, the Cr a_{1g} $3d$ AO does not change its energy in the complex.

In accordance with perturbation theory, the shift by 1 eV of the Cr e_{2g} d-AOs with respect to the unperturbed a_{1g} level is accompanied by a destabilization of the e_{2g} π^* vacant level by the same value. The gap between a_{1g} and e_{1g} Cr d-AOs can be estimated in the same way, on the basis of the position of the π-MOs in dibenzenechromium. The experimental value of the mass centre of the broad π-band in the PE spectrum of the $(C_6H_6)_2Cr$ complex is 9.6 (± 0.1) eV. The position of the e_{1u} π-level determined by us is at 9.46 eV. Assuming that the broad symmetric band in the PE spectrum of $(C_6H_6)_2Cr$ consists of two equidistant bands, we obtain for the energy of e_{1g} π-MO a value equal to 9.74 eV. The stabilization value of 0.72 eV for the e_{1g} π-MO can be accepted for the destabilization shift of the e_{1g} Cr d-AO in the complex. Thus, we arrive at the following MO sequence in the complex: 9.74 eV for e_{1g} π, 9.46 eV for e_{1u} π, 6.40 eV for e_{1g} d, 5.40 eV for a_{1g} d (occupied orbitals); 4.68 eV for e_{1g} d, 4.29 eV for e_{2u} π^*, 3.47 eV for e_{1g} π^*, vacant orbitals. The authors of ref. 6, who have studied dibenzenechromium by the ETS method, present the following energies for vacant MOs: 4.64 for e_{1g} d, 4.18 eV for e_{2u} π^* and 3.47 eV for e_{2g} π^*. The remarkable coincidence between these experimental MO energy values and ours, points to the correct approach used by us.

Model of electrostatic interaction in the derivatives of dibenzenechromium

The E_0 value corresponding to the difference in the energies of the atom terms in the ligand field and in its absence is not calculated in crystal field theory. E_0 does not depend on the symmetry of the d-orbitals and is determined by the spheric part of the potential produced by the ligands at the location site of the metal atom [13]. Let us assume, as accepted in crystal field theory, that the charges are localized at

Table 2

Molecular electrostatic potential (MEP) and E_0 values for (arene)(arene′) and ionization potentials (IP) of (arene)Cr(arene′)

arene, arene′	φ_1(V)	φ_2(V)	E_0(eV)	$IP_1^{calc.}$(eV)	$IP_1^{exp.}$(eV)
$(C_6H_6)_2$	−0.657	−0.657	−1.315	5.400	5.40
$C_6H_5CN, C_6H_5CH_3$	−0.167	−0.748	−0.915	5.800	5.73
C_6H_5CN, C_6H_6	−0.168	−0.671	−0.839	5.876	5.85
C_6H_5CN, C_6H_5Cl	−0.193	−0.362	−0.555	6.160	6.09
C_6H_5CN, C_6H_5F	−0.194	−0.273	−0.467	6.248	6.14
$(C_6H_5CN)_2$	−0.199	−0.199	−0.398	6.317	6.41
$(C_6H_5CF_3)_2$	−0.0865	−0.0865	−0.173	6.542	6.10
$(C_6H_5F)_2$	−0.264	−0.264	−0.528	6.187	5.91
$(C_6H_5Cl)_2$	−0.377	−0.377	−0.755	5.960	5.90
$(m\text{-}Cl_2C_6H_4)_2$	−0.104	−0.104	−0.208	6.507	6.20
$(p\text{-}F_2C_6H_4)_2$	+0.155	+0.155	+0.311	7.026	6.38
$(p\text{-}FC_6H_4CF_3)_2$	+0.308	+0.308	+0.616	7.332	6.58
$[m\text{-}(CF_3)_2C_6H_4]_2$	+0.395	+0.395	+0.790	7.506	6.70
$(C_6H_5CH_3)_2$	−0.728	−0.728	−1.456	5.258	5.31
$[o\text{-}(CH_3)_2C_6H_4]_2$	−0.793	−0.793	−1.586	5.129	5.21
$[1,3,5\text{-}(CH_3)_3C_6H_3]_2$	−0.848	−0.848	−1.696	5.019	4.97
$[1,2,3\text{-}(CH_3)_3C_6H_3]_2$	−0.854	−0.854	−1.708	5.006	5.04
$[1,2,4,5\text{-}(CH_3)_4C_6H_2]_2$	−0.916	−0.916	−1.832	4.882	4.85

points coinciding with the nuclei of the corresponding atoms. In that case, the molecular electrostatic potential in the point charge approximation model (MEP PC) for the $(C_6H_6)_2$ symmetry centre (the atom metal location) is expressed by

$$\varphi = \sum_{i=1}^{N} \frac{q_i}{r_i} \tag{5}$$

formula 5 where N denotes the number of atoms in $(C_6H_6)_2$, q_i denotes the charges on the atoms, and r_i denotes the distance from the symmetry centre to the corresponding ligand atom. The energetic shift of the central atom terms due to the presence of such a potential is expressed by eq. 6 where e is the electron charge. In

$$E_0 = e \cdot \varphi \tag{6}$$

particular, the values for the charges on the C and H atoms in $(C_6H_6)_2$ according to MNDO calculations are −0.0575 and +0.0575e, respectively, and $E_0 = -1.32$ eV. The introduction of substituents leads to a redistribution of electron density in the ligands and, consequently, changes the potential value and E_0.

The MNDO method was applied for calculations involving (arene)(arene′) species. The calculation results of the inductive E_0 shifts for these systems and corresponding MEP PC are listed in Table 2. φ_1 and φ_2 are MEP values due to each of the arene ligands. If we accept the dibenzenechromium molecule as the "reference point", we can obtain an IP vs. MEP expression (eq. 7) where IP_1^0 is the first IP

$$IP_1^{calc.}(R) = IP_1^0 + E_0(R) \tag{7}$$

of the complex whose ligands provide a zero φ potential at the Cr atom location site and R denotes the substituent type in the ligands. Hence, eq. 8 follows.

$$IP_1^0 = 5.4 - (-1.32) = 6.72 \text{ eV} \tag{8}$$

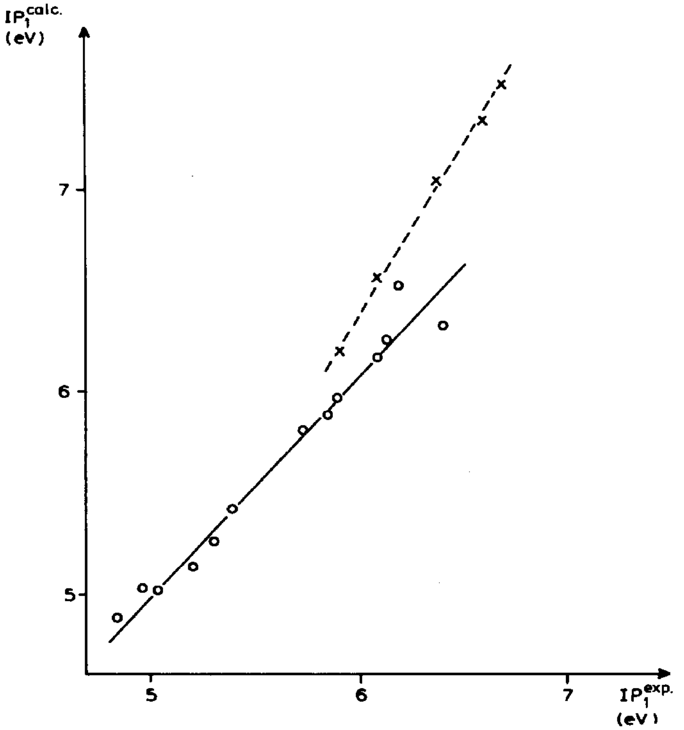

Fig. 3. Correlation dependence between calculated and measured IP_1, The crosses denote F-containing molecules. The points indicate the remaining molecules (see Table 2).

The $IP_1(R)$ values calculated from formula 7 and experimental data (II–VII from this work, the rest from ref. 5) are tabulated in Table 2. Analyses of the φ_1 values for molecules of type $(C_6H_5CN)(C_6H_5R)$ (R = CH_3, H, Cl, F, CN) have shown that the MEP produced by the benzonitrile ligand is practically independent of the character of the substituent in the second ring. The change in E_0 does not exceed 0.03 eV. In other words, $\varphi = \varphi_1 + \varphi_2$ is an additive value. The separate contribution of the ligands can be calculated independently.

The dependence between calculated (according to formula 7) and experimental IPs is given in Fig. 3. The correlation coefficient for the 18 compounds tabulated in Table 2 is 0.966. However, if the group of symmetrically substituted bis-arene-chromium complexes with substituents F and CF_3 is singled out from the set of data, the correlation coefficient is 0.999 for the fluorine-containing compounds and 0.986 for the remainder.

For the fluorine-containing complexes, the correlation equations relating $IP_1^{exp.}$ (R) to the MEP theoretical value assumes the form shown in eq. 9 while for the

$$IP_1^{exp.}(R) = 6.21 + 0.601 \cdot \varphi(R), \tag{9}$$

other compounds it is given by eq. 10.

$$IP_1^{exp.}(R) = 6.58 - 0.906 \cdot \varphi(R) \tag{10}$$

Apparently, the calculations in the MNDO approximation systematically overestimate the q_i value for ligands containing fluorine atoms.

The high correlation coefficients for the series of molecules involved indicate that the method for estimating E_0 values in the bis-arene-chromium complex series is correct. It allows determination, with a high degree of precision, of the first IP of the unstudied complexes. Besides, this strongly confirms the predominantly inductive influence of substituents on the electronic shell of the Cr atom [9]. It should be noted that the possible conjugation effects of the substituent orbitals with π^*-MO of the e_{2g}-symmetry cannot substantially contribute to the *d*-orbital energy. This is evidenced by the constant width of the second PES band for the whole series of molecules. The absence of its splitting and nearly constant separation from the first a_{1g} band of *d*-AO, equal to 1 eV, points to a uniformity of the ligand field in the whole series.

Thus, we can present a brief review of the method for calculating the electronic structure of bis-arene-chromium complexes.

According to the MNDO method or any other method capable of adequately reproducing the sequence of levels and the separation between them, it is possible to calculate the (arene)(arene′) species consisting of ligands of the molecule under study. After correcting the position of the energy levels according to PES data of free ligands and determining the position of the chromium *d*-AO in the ligand field by calculating the MEP PC, it is possible to construct the energy level diagram of the complex using first-order perturbation theory. In contrast to the traditional approach of crystal field theory, this method involves establishing E_0, which is the energy difference between the states of the chromium atom in the complex and in the absence of the electrostatic field. It is to be noted that the influence of substituents on the highest occupied MOs of bis-arene-chromium complexes, mirrored by the existence of linear dependences of types 1, 3 and 10, is due to purely electrostatic interaction.

Experimental and quantum chemical calculations

Synthesis of unsymmetrical complexes is described in refs. 14–17. The purity of the compounds was controlled by mass spectroscopy.

The He-I photoelectronic spectra were obtained on an electron spectrometer ES 3201 supplied with a heated inlet system. The typical working resolution was 40 meV. The PE spectra were calibrated against the $^2P_{3/2}$ and $^2P_{1/2}$ Xe lines. The uncertainty values of the ionization potentials were ± 0.02 eV for IP_1 and ± 0.05 eV for higher IPs.

The quantum chemical calculations of the (arene)(arene′) species were carried out using the MNDO method with optimization of C–R bond lengths. The C–C and C–H bond lengths in the arene rings were chosen to be 1.40 and 1.10 Å, respectively. Optimized bond lengths were found to be 1.7509 Å for C–Cl and 1.3290 Å for C–F; for the C–CN groups, the C–C bond length is 1.4319 Å and C≡N is 1.1619 Å; for the $C-CF_3$ groups, the C–C bond length is 1.527 Å, C–F is 1.3577 Å and angle CCF is 112.92°; for the $C-CH_3$ groups, the C–C bond length is 1.5184 Å, C–H is 1.10 Å and angle CCH is 110.0°; for the $C-OCH_3$ groups, the C–O bond length is 1.41 Å, $O-CH_3$ is 1.395 Å, C–H is 1.10 Å and angles COC are 118.6° and 110.0°.

References

1 M.P. Guest, I.N. Hiller, B.R. Higginson and D.R. Lloyd, Mol. Phys., 29 (1975) 113.
2 M.C. Böhm, J. Chem. Phys., 78 (1983) 7044.
3 S. Evans, J.C. Green and S.E. Jackson, J. Chem. Soc. Dalton, 3 (1973) 304.
4 J. Weber, E.P. Kündig, A. Coursot and E. Penigault, Can. J. Chem., 63 (1985) 1734.
5 D.E. Cabelli, A.H. Cowley and J.J. Lagowski, Inorg. Chim. Acta, 57 (1982) 195.
6 P.D. Burrow, A. Modelli, M. Guerra and R.D. Jordan, Chem. Phys. Lett., 118 (1985) 328.
7 V.G. Zakzhevsky, Information materials from the quantum-chemical programs fond of the Siberian department of the USSR Academy of Sciences, 2nd issue, SFKP-59, Novosibirsk, 1980, Program Calculation.
8 A.J. Gordon and R.A. Ford, The Chemist's Companion, John Wiley and Sons, New-York-London-Sydney-Toronto, 1972.
9 L.P. Yur'eva, S.M. Peregudova, L.N. Nekrasov, A.P. Korotkov, N.N. Zaitseva, N.V. Zakurin and A.Yu. Vasil'kov, J. Organomet. Chem., 219 (1981) 43.
10 A. Haaland, Acta Chem. Scand., 19 (1965) 41.
11 J.A. Barltrop and J.D. Coyle, Excited States in Organic Chemistry, John Wiley and Sons, London, New York, Sydney, Toronto, 1975.
12 R. Krishnamurthy and W.B. Schaap, J. Chem. Educ., 46 (1969) 799.
13 I.B. Bersuker, Structure and Properties of Coordination Compounds, Khimiya, Leningrad, 1971, p. 312.
14 A.N. Nesmeyanov, V.A. Sergeev, N.V. Zakurin, A.Yu. Vasil'kov, A.S. Kogan, L.P. Yur'eva, N.N. Zaitseva and I.A. Uralets, J. Organomet. Chem., 217 (1981) 195.
15 A.Yu. Vasil'kov, N.V. Zakurin, I.A. Uralets, N.N. Zaitseva, N.I. Vasyukova, A.G. Makarovskaya and L.P. Yur'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1982) 2144.
16 V.A. Sergeev, A.S. Kogan, I.A. Uralets, A.Yu. Vasil'kov, N.V. Zakurin and L.P. Yur'eva, Izv. Akad. Nauk SSSR, Ser. Khim., (1984) 420.
17 V.A. Sergeev, A.S. Kogan, A.Yu. Vasil'kov, I.A. Uralets, N.N. Zaitseva, L.P. Yur'eva and D.N. Kravtsov, Izv. Akad. Nauk SSSR, Ser. Khim., (1986) 237.