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Ab initio calculations of the charge densities in tricarbonyl(boat *p*-xylene)chromium complexes

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Abstract

Ab initio SCF calculations predict that the charge densities on the aryl carbons of Cr(boat *p*-xylene)$(CO)_3$ and also the difference in charge density from the free boat *p*-xylene are dependent on the degree of deformation of the boat. This prediction is consistent with the observed geometry-dependent ^{13}C NMR complexation shifts of Cr(paracyclophane)$(CO)_3$ complexes.

Introduction

Complexations of arenes with transition metals cause large upfield shifts of ^{13}C NMR peaks for the aryl carbons. One of us has recently found that the complexation shift in Cr, Fe, Mo and Ru complexes of paracyclophanes is dependent on the angle of bending of the aryl ring [1–5]. This dependence has no direct relation to magnetic anisotropy and/or field effects of the metal moiety, transannular electronic effects and ring-current effect [1,2]. It seems of interest to seek its origin on a theoretical base. Thus by use of an ab initio SCF MO approximation we have examined whether the difference in charge density between a boat-deformed *p*-xylene and its $Cr(CO)_3$ complex is dependent on the degree of ring deformation. We report here the results as compared with the observed ^{13}C NMR complexation shifts of Cr(paracyclophane)$(CO)_3$ complexes.

Calculations

Ab initio SCF calculations were carried out with the GSCF3 program [6] on a HITAC M-680H computer at the Computer Centre of the University of Tokyo. The basis sets employed in this calculation were a linear combination of Gaussians. The minimal STO-3G basis sets were used for H, C, and O atoms, and the Gaussian basis set $(14s8p5d)/[5s3p1d]$ was used for Cr atom. The $Cr(CO)_3$ structure parameters used were those taken from ref. 7. The usual *p*-xylene structure was used, modified as follows:

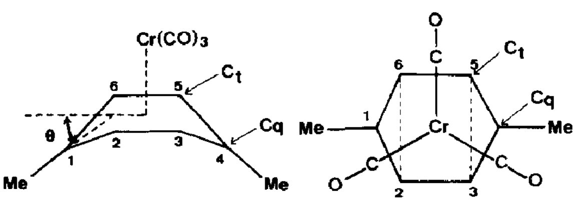

Fig. 1. Molecular geometry of Cr(boat *p*-xylene)(CO)$_3$ used in the ab initio calculations.

As models for paracyclophanes, various boat conformations of *p*-xylene were used so as to keep the computational time for their complexes as short as possible. *p*-Xylene was bent into a boat by displacement of the quaternary C_1 and C_4 atoms (C_q) out of the plane of the tertiary C_2, C_3, C_5 and C_6 atoms (C_t) at bending angles (θ) of 0 ~ 20°, as shown in Fig. 1. In this case, the C_1–Me bond and the aryl hydrogens were fixed to lie in the planes $C_1C_2C_6$ * and $C_2C_3C_5C_6$ **, respectively. Moreover, the boat *p*-xylene was assumed to have C_{2v} symmetry. In the Cr(boat *p*-xylene)(CO)$_3$ complexes, it was assumed that the ligand boat *p*-xylene has the same structure as that of the uncomplexed one and that the three CO groups attached to the Cr atom, which is located just above the center of the ring plane, are oriented above the middle points of the three bonds C_1–C_2, C_3–C_4 and C_5–C_6, as in the crystal structure of Cr([2.2]paracyclophane)(CO)$_3$ [7]. Under these assumptions, optimization of the distance between the Cr and the plane of $C_2C_3C_5C_6$ gave a total energy minimum at 1.82Å. The charge densities calculated for two C_q, four C_t and three carbonyl C atoms were averaged separately.

Results and discussion

Table 1 shows the ab initio charge densities (q) in boat *p*-xylenes and their Cr(CO)$_3$ complexes. In the uncomplexed *p*-xylenes, C_q has a positive q value which

Table 1

Calculated charge densities (q) [a] in *p*-xylene and in its Cr(CO)$_3$ complex.

Bending angle (θ (°))	Free *p*-xylene		Cr(CO)$_3$ complex				
	C_t	C_q	C_t	C_q	Cr	C(C=O)	O(C=O)
0	−0.0682	+0.0096	−0.2050	−0.0464	+1.2251	+0.0549	−0.2273
5	−0.0683	+0.0098	−0.2090	−0.0353	+1.2179	+0.0560	−0.2282
10	−0.0686	+0.0101	−0.2124	−0.0255	+1.2064	+0.0582	−0.2287
15	−0.0691	+0.0107	−0.2148	−0.0168	+1.1935	+0.0602	−0.2294
20	−0.0698	+0.0114	−0.2167	−0.0090	+1.1816	+0.0626	−0.2299

[a] q is given by 6 − Q(C), 8 − Q(O) or 24 − Q(Cr), where Q(A) denotes the population on atom A.

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* Our preliminary CNDO/2 calculations predicted that displacement of Me out of the $C_1C_2C_6$ plane has no substantial influence on q for C_q and C_t [8].

** MINDO/2 calculations predicted that, in a boat benzene with C_1 and C_4 being displaced out of the basic plane of $C_2C_3C_5C_6$ by 13°, the aromatic H_2, H_3, H_5, and H_6 atoms lie nearly on the basic plane [9].

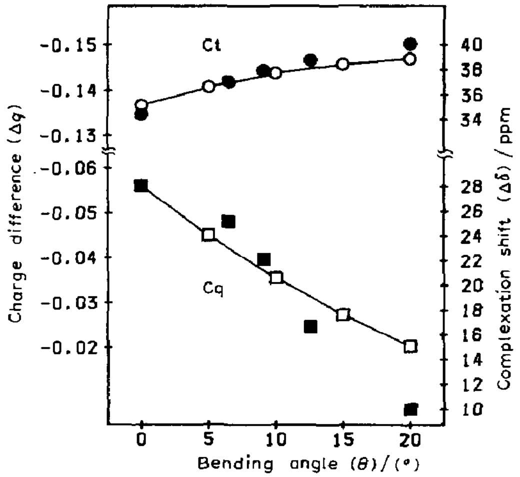

Fig. 2. Plots of calculated charge differences (Δq) (open) and observed complexation shifts ($\Delta\delta$) (closed) against bending angle (θ), where $\Delta q = q$(complex) − q(hydrocarbon) and $\Delta\delta = -[\delta$(complex) − δ(hydrocarbon)].

changes from +0.0096 to +0.0114 as θ increases, but C_t shows a negative q value which scarcely changes with θ. In the complexes, C_t and C_q show larger negative q values than those in the uncomplexed ones, and q for C_q is remarkably angle-dependent compared with that for C_t. As a result, the difference in q (Δq) for C_t in the boat *p*-xylene and in its complex decreases slightly, whereas that for C_q increases substantially with increases in θ, as is shown in Fig. 2. Moreover, the figure shows that the opposite trends in Δq for both C atoms are consistent with the geometry-dependent ^{13}C NMR complexation shifts ($\Delta\delta$) observed for C_t and C_q in Cr(arene)$(CO)_3$ complexes, where the arene ligand is either *p*-xylene (θ 0°), [3.3]paracyclophane (6.4° [10]), [8]paracyclophane (9° [11]), [2.2]paracyclophane (12.6° [12]) or [6]paracyclophane (20° [13]). To plot $\Delta\delta$ against θ, the θ values used are those taken from the X-ray diffraction data for the uncomplexed cyclophanes and the $\Delta\delta$ values (in $CDCl_3$) were taken from the literature [3], except for the unpublished data for Cr([3.3]paracyclophane)$(CO)_3$ [14*] and Cr([6]paracyclophane)$(CO)_3$ [15*].

Finally, it is noted that in the complexes, q for Cr is always positive and decreases as θ increases. This result predicts that back-donation [16] by the Cr atom to the aryl ring is angle-dependent. With increase in θ, back-donation becomes weaker, such that donation to C_q is decreased significantly, but the donation to C_t is slightly increased.

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