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THE INFLUENCE OF SUBSTITUENTS ON THE STRUCTURE OF DICOBALT OCTACARBONYL. A THEORETICAL INVESTIGATION

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Summary

The effect of the substituents on the flap angle of the inner ring in $Co_2(CO)_8$ was investigated using EHT calculations. Ethylene, *cis*-butadiene and cyclopentadienyl anion were considered as replacements for the terminal carbonyls. The results show the *trans* isomers to be planar, unlike the *cis* isomers in which the ring puckering is dependent on the nature of the substituents. It is predicted that the interconversion of *cis*—*trans* tautomers takes place through ring opening.

Introduction

The structure and reactivity of dicobalt octacarbonyl ($Co_2(CO)_8$) have been investigated in recent years both by spectroscopic techniques and theoretical calculations. The interest in this complex is mainly due to its use as a catalytic precursor in the hydroformylation of olefins [1].

The crystal structure of the complex IA, determined by X-ray diffraction [2], shows two bridging carbonyls; the inner ring formed with the Co atoms is not planar, but highly puckered ($\theta = 127°$). Moreover there is spectroscopic evidence for "open" isomers in solution and under hydroformylation conditions [3].

In one of our recent papers [4] the structures of both the open and bridged forms were investigated by theoretical calculations, which were used to interpret the changes in the IR spectrum observed upon temperature variations. Recently Hoffmann and Pinhas [5] made a detailed analysis of the "ring puckering" and metal—metal separation in a series of dibridged binuclear complexes, especially $Co_2(CO)_8$.

From studies of the IR spectra of dienedicarbonylcobalt dimer complexes [6], McArdle and Manning showed that these compounds contain planar rather than puckered inner bridges. The *cis*—*trans* tautomerism observed was found to be partly solvent dependent; some complexes exist in solution solely as *trans* or *cis* isomers, and others as mixtures of the two.

The crystal structure of a sodium salt of the binuclear radical anion cyclopentadienylcobaltcarbonyl dimer $[Co(CO)Cp]_2^-$, determined by X-ray diffraction [7], shows that the cobalt atoms and the bridging carbonyls are coplanar to better than 0.01 Å, and the mean intermetallic distance is 2.36 Å, surprisingly short when compared with the corresponding distance in IA, viz. 2.52 Å. The occurrence of only one stretching mode in the spectrum of the corresponding neutral complex $[Co(CO)Cp]_2$ suggests a similar planar geometry for the inner ring [8].

In the present paper a theoretical investigation is made of the bridged $Co_2(CO)_8$ and its derivatives obtained by replacement of carbonyls by unsaturated moieties. The Extended Hückel Theory (EHT) method [9] was employed for the calculations; this method was satisfactorily used in previous studies on cobalt carbonyl complexes [4,5]. In particular, this simple computing technique allows optimization of the geometry of these large complexes by taking account of the largest possible number of geometrical variables in a reasonably limited computing time. The main purpose of the present investigation was to probe the influence of substituents on the ring puckering of $Co_2(CO)_8$, through direct minimization of the total energy of the example considered.

Method of calculation

According to the EHT method [9] the diagonal matrix elements H_{ii} correspond to the valence state ionization potentials, and the values adopted, already used in a previous investigation [4], as well as the other parameters employed, are reported in Table 1. Off-diagonal elements H_{ij} were computed from the Wolfsberg-Helmholtz equation [10].

The total energy of each complex was optimized as a function of all the angular parameters and of the cobalt—cobalt distance, taking account of whether or not the removal of symmetry constraints might lead to lower energy values. The Powell method [11], based on conjugated directions, was employed for automatic optimization of the geometrical parameters.

Results and discussion

$Co_2(CO)_8$

Table 2 shows a list of total energies and geometrical parameters for the

TABLE 1

PARAMETERS USED IN THE EHT CALCULATIONS

	Slater exponents	H_{ii} (eV)
C	1.62 (2*s*, 2*p*)	−23.0 (2*s*), −13.4 (2*p*)
O	2.28 (2*s*, 2*p*)	−33.9 (2*s*), −16.4 (2*p*)
H	1.30 (1*s*)	−13.6 (1*s*)
Co	2.00 (3*d*)	−17.9 (3*d*)
	1.60 (4*s*, 4*p*)	−8.0 (4*s*, 4*p*)
		$K = 1.80$

eclipsed bridged isomer IA, optimized by EHT and CNDO/2 [12] methods making use of detailed investigation on the bridged and open structures of $Co_2(CO)_8$ in the gas phase [4]. Total energy and MO's calculated with a different set of CNDO parameters for its experimental geometry are available in the literature [13]. The fairly close agreement between the geometrical parameters optimized by EHT and the experimental values, shown in Table 2, induced us to employ this computational technique to investigate the stability of a possible staggered structure IB for bridged $Co_2(CO)_8$. In fact, as mentioned above, *cis—trans* tautomerism of dienedicarbonylcobalt complexes has been demonstrated by IR spectroscopy [6]. The total energy and optimized geometrical parameters for the staggered isomer are also shown in Table 2. It can be seen that this isomer is planar ($\theta = 180°$) unlike the eclipsed form, which is predicted to be highly puckered by EHT ($\theta = 130°$; $\theta_{\exp} = 127°$). The former is about 20 kcal mole^{-1} ($\Delta E = 0.87$ eV) less stable, and the Co—Co distance is moderately longer (stag.: 2.60 Å; eclip.: 2.56 Å; exp. (eclip.): 2.52 Å). However the mean distance is significantly shorter than the corresponding distances in the open structures (2.87 and 2.88 Å for the structures of D_{4h} and D_{3d} symmetry, respectively [4]).

The trend of HOMO's and LUMO's of IA vs. the angle of puckering θ (Walsh diagrams) shown in Fig. 2, is almost independent of θ, the inversions of HOMO′ (b_2) and HOMO″ (a_2) at about $\theta = 100°$, and of HOMO^{IV} (a_1) and HOMO^{V} (b_1) at about $\theta = 160°$ being the only two exceptions. The Walsh diagram for IB is reported in the same figure. In this case the inversion of HOMO′ (a′) and HOMO″ (a″) occurs at about $\theta = 120°$, and that of the two LUMO's at $\theta = 125°$.

Comparison of our Walsh diagram for IA with the corresponding diagram

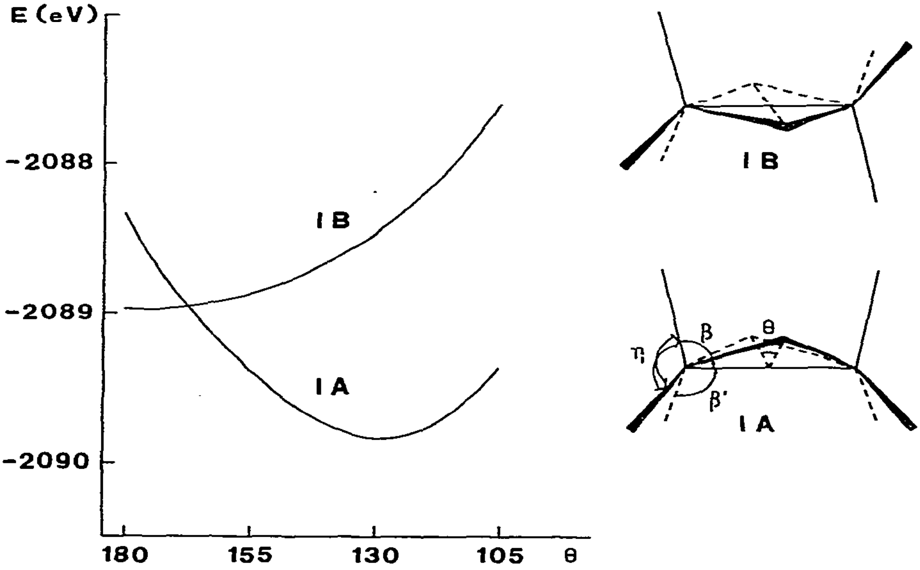


Fig. 1. Total energies vs. flap angle θ and structures of eclipsed IA and staggered IB isomers of $Co_2(CO)_8$.

TABLE 2

TOTAL ENERGIES, AND EXPERIMENTAL AND OPTIMIZED GEOMETRICAL PARAMETERS FOR STAGGERED AND ECLIPSED BRIDGED ISOMERS OF $Co_2(CO)_8$

		Symmetry	Co—Co (Å)	Co—C_T (Å)	C_T—O_T (Å)	Co—C_B (Å)	C_B—O_B (Å)	θ [d] (°)	β (°)	β' (°)	η (°)	Energy (eV)
IA	Experimental [a]	C_s	2.52	1.80	1.17	1.90	1.20	127	116	109 124	113, 122	
	EHT	C_{2v}	2.56	1.80 [c]	1.17 [c]	1.80 [c]	1.17 [c]	130	119	116	127	−2089.95
	CNDO/2 [b]	C_{2v}	2.34	1.78	1.25	1.99	1.30	122	117	110	120 [c]	−6786.04
IB	EHT	C_{2h}	2.60	1.80 [c]	1.17 [c]	1.80 [c]	1.17 [c]	180	104	124	125	−2088.98

[a] Ref. 2. [b] Ref. 12. [c] Assumed value. [d] θ, β, β', η as indicated in IA and IB.

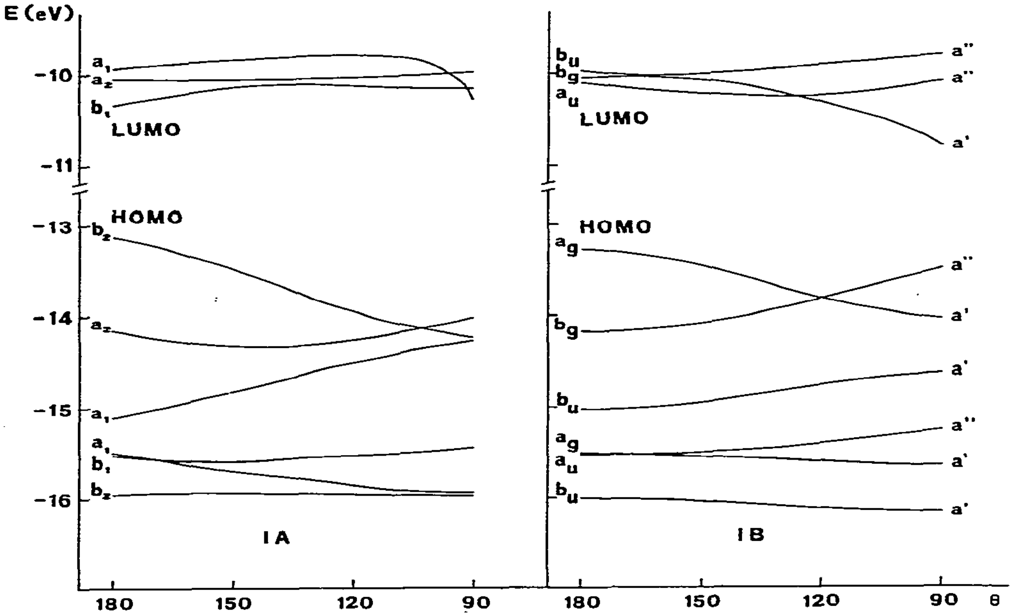


Fig. 2. HOMO's and LUMO's energies vs. θ for IA and IB.

given by Hoffmann and Pinhas [5] shows that the trend for each corresponding MO is qualitatively similar, whereas the relative ordering of the MO's does not appear to be the same in the two diagrams. We ascribe the different ordering of MO's to the different set of parameters used in the two calculations. However, it is noteworthy that both calculations satisfactorily predict the angle of puckering of the inner ring of IA (θ = 143° in ref. 5; θ = 130° in ref. 4; θ_{exp} = 127° [2]).

The reason why EHT calculations correctly predict the inner ring of IA to be puckered and suggest that of IB to be planar can be explained by the sequence of the two first HOMO's vs. θ (Fig. 2). In the case of IA, HOMO' (b_2) and HOMO" (a_2) favour the distortion of the ring from planarity, unlike IB, in which the two first HOMO's (a', a'') exhibit an opposite trend: HOMO' (a') is destabilized as the ring puckers, while HOMO" (a'') tends to retain a planar structure for the complex.

As for the interconversion path between IA and IB, it can be observed that the energies of the open structures, reported in Table 2 of ref. 4, are higher than those of the bridged isomers. In the same paper the pathway for the interconversion process from IA to the stable open isomers was also described. Both the relative values of the energies of the different isomers and the way the bridge opening occurs suggest that the eclipsed/staggered interconversion occurs through the opening of the ring, so that the open structures are intermediates in the process.

[Co(CO)$_3$Et]$_2$ (Et = ethylene)

In order to make a systematic investigation of the effect of replacement of

TABLE 3

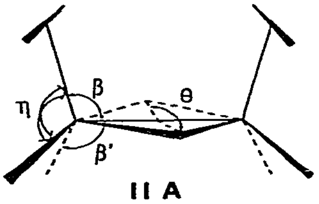
ENERGIES AND OPTIMIZED GEOMETRICAL PARAMETERS FOR *cis* AND *trans* ISOMERS OF $Co_2(CO)_nL_2$

(L: Et = Ethylene; Bu = *cis*-Butadiene; Cp = Cyclopentadienyl) [a]

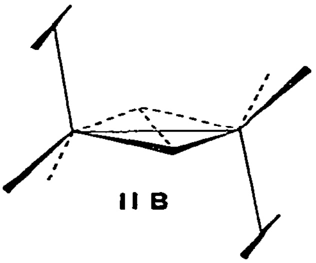
		Struct.	Electronic conf.	Energy (eV)	Co—Co (Å)	θ (°)	β (°)	β' (°)	η (°)
$Co_2(CO)_8$	eclipsed	IA	d^9—d^9	−2089.95	2.56	130	119	116	127
	staggered	IB		−2088.98	2.60	180	104	124	125
$[Co(CO)_3Et]_2$	*cis*	IIA	d^9—d^9	−2116.63	2.71	172	105	122	127
	trans	IIB		−2116.72	2.68	180	100	126	125
$[Co(CO)_2Bu]_2$	*cis*	IIIA	d^9—d^9	−2076.02	2.60	152	127	108	—
	trans	IIIB		−2075.78	2.58	180	128	104	—
$[Co(CO)Cp]_2^{2-}$		IV^{2-}	d^9—d^9	−1787.07	2.54	112	159	—	—
$[Co(CO)Cp]_2^-$		IV^-	d^8—d^9	−1774.87	2.49	180	180	—	—
$[Co(CO)Cp]_2$		IV	d^8—d^8	−1764.21	2.34	180	180	—	—

[a] Ethylene: C—C = 1.35 Å, C—H = 1.10 Å; butadiene: C—C = 1.46 Å, C—H = 1.09 Å, Co—Bu distance (1.78 Å) was optimized; cyclopentadienyl: C—C = 1.399 Å, C—H = 1.09 Å, Co—Cp = 1.74 Å. Other assumed values: Co—C = 1.8 Å and C—O = 1.17 for carbonyls.

carbonyl ligands by unsaturated organic moieties on the puckering of the inner bridges of IA and IB, a complex obtained by substitution of two carbonyls by two ethylene fragments (as far as we know, unknown) was first studied. Of the various disubstituted isomers considered, only the *cis* IIA and *trans* IIB tautomers of highest symmetry, C_{2v} and C_{2h}, respectively, are discussed.



II A



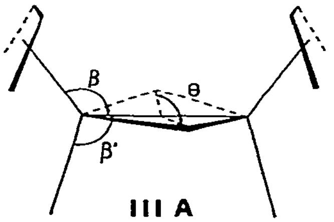
II B

The Co—Co distance and the angular variables shown above were included in the energy optimization process. The parameters compatible with the energy minima are shown in Table 3. It appears that the geometries of the two isomers are slightly different. In particular, the inner ring is planar ($\theta = 180°$) for *trans* IIB, while the ring of *cis* IIA is predicted to be slightly puckered ($\theta = 171.7°$). The former turned out to be 7—8 kcal mol^{-1} more stable than the latter.

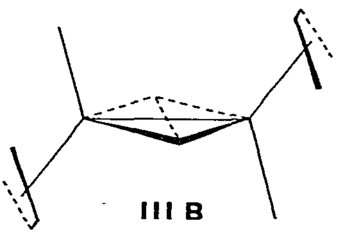
The remarkable change in the ring puckering in IIA ($\Delta\theta = 42°$) compared with that in the unsubstituted IA is notable; in contrast, the conformation of the ring of IIB remained unchanged after substitution. The Co—Co distance lengthens by about 0.1 Å in both isomers.

[Co(CO)$_2$Bu]$_2$ (Bu = cis-butadiene)

This complex is the simplest in a series derived from I when four terminal carbonyls are replaced by two diene moieties. *cis*-Butadiene was therefore used as the substituent and both the geometry and the relative stability of the isomers IIIA and IIIB investigated.



III A



III B

The total energies and optimized geometrical parameters are summarized in Table 3. It appears that the *cis* isomer is 5—6 kcal mol^{-1} more stable than the *trans* isomer. As in the case of IIA and IIB, most of the geometrical parameters of the two complexes are very similar. The only substantial difference lies in the conformation of the inner ring, which is planar for *trans* IIIB and significantly puckered ($\theta = 152°$) for *cis* IIIA. Comparison with the unsubstituted and disubstituted complexes shows that the ring of the *trans* tautomers is planar and unaffected by the substituents. In contrast, in the case of *cis* tautomers, the ring puckering is directly dependent on the nature of the substituent and on the effect of the substituent on the ordering of the cobalt MO's.

$[Co(CO)Cp]_2^{z-}$ (z = 2, 1, 0; Cp = cyclopentadienyl)

If the standard isolobal replacement of three carbonyls by a cyclopentadienyl moiety (Cp^-) is made, the title complex IV^{2-} is obtained with $z = 2$. The electron configuration of the Co atoms is d^9—d^9, the same as in the unsubstituted and substituted complexes previously examined.

To our knowledge the crystal structure of IV^{2-} has not been reported in the literature, unlike that of the monoanion IV^-. The neutral complex IV is also known as a solid which is slowly converted into the unsoluble trimer $[Co(CO)Cp]_3$ in solution [8]. Its crystal structure is unknown, but the appearance of only one stretching mode in the IR spectrum indicates a coplanar geometry for the central ring [8], as mentioned in the Introduction.

The total energy and optimized geometrical parameters for IV^{2-}, IV^- and IV

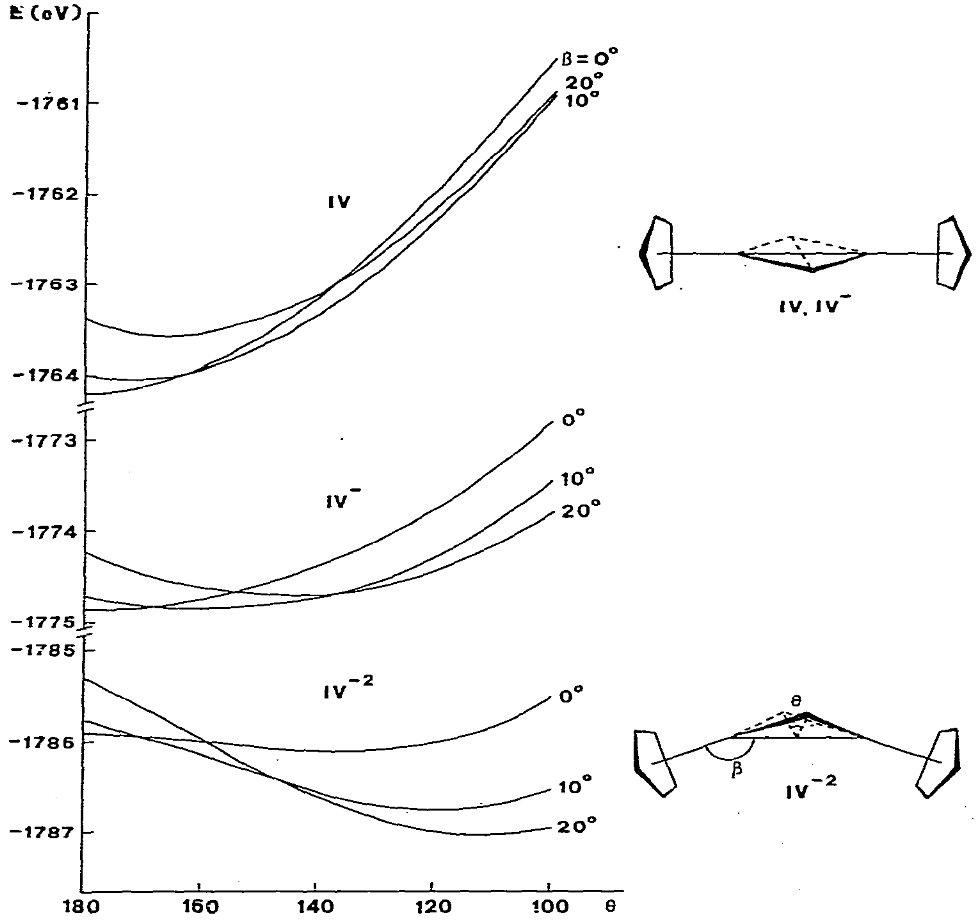


Fig. 3. Total energies vs. θ with different β values, and structures of the dianion IV^{2-}, monoanion IV^- and the neutral complex IV of $[Co(CO)Cp]_2$.

are given in Table 3. The significant puckering (θ = 112°) of the inner ring of IV^{2-} predicted by our EHT calculations is surprising, as it is known that in the Cp_2M_2AB series (M = Fe, Co, Ni; A, B = CO, NO) a planar structure is preferred, as pointed out by Hoffmann and Pinhas [5]. However, the inner ring of $[CpNi(CO)]_2$ is puckered (θ = 138–142° [14]).

It should be observed that the present calculations accurately predict the planarity of the inner rings of the monoanion IV^- and the neutral complex IV, proved by experimental evidence [7,8]. The choice of the set of starting EHT parameters (Co ionization potentials) can, of course, be critical, but analysis of the frontier orbitals of IV, IV^- and IV^{2-}, and in particular of the HOMO's b_2, a_2 and a_1 vs. θ at different values of β (as defined in IV^{2-}) elucidates the relationship between the ring puckering in the three complexes (Fig. 4).

The HOMO′ (b_2) is strongly stabilized as θ decreases, unlike HOMO″ (a_2) and HOMO‴ (a_1) which are destabilized. In the case of IV^{2-} where HOMO′ (b_2) is completely filled, a puckered ring conformation is evidently favoured, independently of other factors. Conversely, in the case of the neutral IV, the aforementioned MO (b_2) is vacated and HOMO′ (a_2) and HOMO″ (a_1) are strongly stabi-

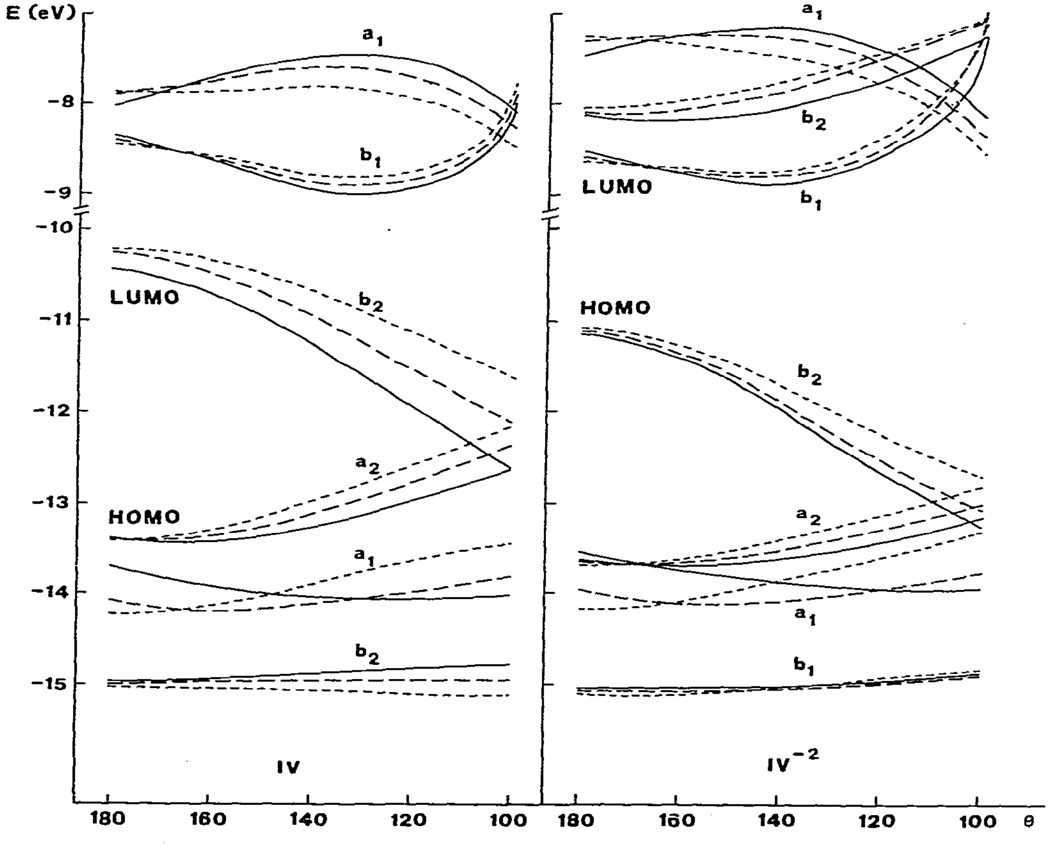


Fig. 4. HOMO's and LUMO's energies vs. θ for IV^{2-} and IV with different β values. β = 180° : - - - - - -; β = 170° : — — —; β = 160° : ———. The similar corresponding diagram for IV^- is omitted.

lized by ring planarity. Lastly, in the case of the monoanion IV^- the presence of only one electron in HOMO′ (b_2) reduces the contribution of this MO to the total energy of the system, so that the monoanion should show a greater preference for a planar inner ring than the dianion and a lower preference than the neutral complex. This is clearly evidenced by the variations of the total energies with θ shown in Fig. 3.

Concluding remarks

EHT calculations of the geometries for the eclipsed and staggered form of $Co_2(CO)_8$ provide evidence for the stability of both isomers, correctly predict that the former is puckered, and suggest that the latter is planar, with ΔE = 20.12 kcal mol^{-1} in favour of the eclipsed isomer. When two, four and six carbonyls are replaced by two ethylenes, *cis*-butadienes, or cyclopentadiene anions, the optimized geometries of the tautomers show that the inner ring is planar in the *trans* isomer, while puckered in the *cis* isomer. The magnitude of the flap angle cannot be rationalized in terms of the number of the replaced carbonyls, but depends directly on the nature of the substituents. A comparison between the relative stabilities of the bridged and open isomers of $Co_2(CO)_8$ suggests that *cis*/*trans* isomerism can occur through ring opening. The intermediates in the interconversion of *cis*—*trans* bridged tautomers can thus be expected to be the open form for $Co_2(CO)_8$ and its substituted derivatives.

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