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Molecular and Crystallographic Study of Tropolone Type Derivatives by *ab initio* Hartree–Fock Calculations

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ABSTRACT

The molecular structures of the ground states of tropolone, 3,5,7-tribromotropolone and 5-nitrotropolone have been calculated using Hartree–Fock and MP2 methods with the 6-31G(d,p) basis set. The geometrical parameters obtained by using the HF and MP2 methods showed good agreement with the experimental data. The crystal structure of 3,5,7-tribromotropolone, a highly substituted tropolone compound, was determined to verify and correlate the computational results.

KEYWORDS

Tropolone, 3,5,7-tribromotropolone, 5-nitrotropolone, theoretical, crystallography.

1. Introduction

The development of catalytically active metal complexes depends largely on the associated ligands used in the process.[1] Thus, the study of the fundamental properties of potential ligands has increased significantly over the last decade.[2] Catalytic applications involving the use of a tropolone derivative, utilizing yttrium and rhodium metal centres, have been reported for alkyne hydroamination[3] and asymmetric hydrozilation of acetophenone,[4] respectively. With respect to catalytically active complexes, the rhodium metal centre is of interest in hydroformylation and carbonylation processes. The use of diketone complexes to determine the reactive intermediates in the catalysis cycle led to a host of studies on the β-diketone derivatives (with a bite angle O-Rh-O *ca.* 90°).[5,6,7] By contrast, little or no attention has been devoted to the α-diketone derivatives, and it was only recently observed that the smaller bite angles (O-Rh-O *ca.* 75°) of analogous β-diketone derivatives facilitate the formation of five-coordinated rhodium(I) species,[8,9] both in solution and in the solid state. The smallest bite angles observed for rhodium(I) complexes of tropolone derivatives were *ca.* 77° for a 5-nitrotropolone mono-triphenylphosphine moiety[10] and 66° for a 3,5,7-tribromotropolone bis-triphenylphosphine complex[9] (Table 7).

Theoretical studies have been reported on the base tropolone (HTrop) compound,[11–15] but to date no reported data exist for the functionalized 5-nitrotropolone ($HTropNO_2$) and 3,5,7-tribromotropolone ($HTropBr_3$) compounds. The tropolone molecule has a well-established hydrogen bonding pattern in the solid state, forming both intra- and intermolecular hydrogen bonds.[16] Furthermore, π-π stacking is also common in these systems due to the planar nature of the molecule.[17] This is confirmed in the solid state by the X-ray study of 3,5,7-tribromotropolone, which is presented here. Geometrical parameters thus obtained can also be correlated with the observed solid state tropolonato structures, whether in four-coordinated square planar complexes, as in $[Rh(Trop)(CO)(PPh_3)]$,[18] $[Rh(Trop)(CO)(AsPh_3)]$,[19] $[Rh(Trop)(CO)(PFcPh_2)]$,[20] $[Rh(TropNO_2)(CO)(PPh_3)]$[21] and $[Rh(TropBr_3)(CO)((2,4\text{-di-}^tBuPhO)_3P)]$[8]) or in five-coordinated complexes, like $[Rh(Trop)(CO)(PFcPh_2)_2]$,[9] $[Rh(TropBr_3)(CO)(PPh_3)_2]$[9] and $[Rh(TropBr_3)(CO)(AsPh_3)_2]$.[9] The relative energy differences of the tropolone systems can be compared to determine a possible reactivity scale for use in catalytically active processes.[8,9] Electronic effects are included in the theoretical study to determine the effects of strong electron-withdrawing groups, such as nitro ($HTropNO_2$) and tribromo ($HTropBr_3$) moieties. The three symmetrical tropolone systems were specifically selected to minimize conformer distributions in the solid state or gas phase.

2. Experimental

2.1. Chemicals

Tropolone (Aldrich, 98%), potassium bromide (Aldrich, 99%), bromine (Merck, 99%) and methanol (Merck, 99.5%) were used as received.

2.2. Synthesis of Compound

3,5,7-Tribromotropolone ($HTropBr_3$). The ligand was synthesized *via* a procedure proposed by Doering and Knox.[22] To a solution of tropolone (0.1 g, 0.82 mmol) and water (3.0 mL) at 25°C was added a bromine solution (3.6 mL, 50 mmol). The bromine solution was prepared by dissolving bromine (5.36 g, 0.0335 mol) in potassium bromide (7.5 g, 0.063 mol) in water (50 mL). (Yield: 0.279 g, 95%). Spectroscopic details: see below.

A second more convenient synthetic route has also been employed. To a mixture of tropolone (2.0 g, 0.016 mol) in methanol (40 mL) at 25°C was slowly added a solution of bromine (8.0 g, 0.052 mol) in methanol (20 mL). The resultant solution was stirred for half an hour. Upon evaporation single crystals suitable for X-ray crystallography were obtained. (Yield: 5.6 g, 95%), ^1H NMR (300 MHz, $CDCl_3$): δ 8.3 (s), 9 (s, OH) ppm, ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 (C_1, C_2), 144.3 (C_4, C_6), 124.7 (C_3, C_7), 118.4 (C_5) ppm.

2.3. X-ray Crystallography

Reflection data were collected on a Bruker SMART CCD 1K diffractometer, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) at ambient temperature (293 K). Necessary absorption corrections were performed with the SADABS

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Table 1 Crystal and data collection parameters for $HTropBr_3$.

Empirical formula	$C_7H_3O_2Br_3$
M_r/g mol^{-1}	717.65
T/K	293(2)
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	3.995(5)
b/Å	14.042(5)
c /Å	16.057(5)
α/°	90
β/°	90.281(5)
γ/°	90
V/Å^3	900.8(12)
Z	2
D_c/g cm^{-3}	2.646
μ /mm^{-1}	13.388
F(000)	664
Crystal size/mm	0.44 × 0.12 × 0.06
θ Range for data collection/°	1.27–28.30
Index ranges, hkl	–5 to 5, –17 to 18, –17 to 21
Reflections collected	6193
Independent reflections	4179
R_{int}	0.0329
Completeness to theta (°/%)	26.00/99.60
Absorption correction	Multi-scan
Max, min transmission	0.446, 0.158
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	4179/1/219
Goodness-of-fit on F^2	1.078
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0635$ $wR_2 = 0.1506$
R indices (all data)	$R_1 = 0.0799$ $wR_2 = 0.1613$
Extinction	–
Largest diff. peak; hole /eÅ^{-3}	1.426, –1.659 associated with Br atoms

program.[23] The structure was solved by means of conventional Patterson and Fourier methods, and refined by full-matrix least-squares on F^2 by using SHELX-97[24] in the program suite WinGX.[25] The visualization of crystallographic data after refinement was performed using Diamond.[26] The positions of the hydrogen atoms were calculated as riding on the adjacent carbon or oxygen atoms with bond distances: aromatic C–H = 0.93 Å and hydroxyl O–H = 0.82 Å. Selected special refinement techniques were employed for the $HTropBr_3$ structure showing merohedral twinning character. The BASF and TWIN commands were used in conjunction to solve this structure, and the final twin ratio was 20%. All structures are shown with thermal ellipsoid probability factors of 50%. Crystal data are given in Table 1. CCDC 274169.

2.4. Computational Details

Theoretical calculations were performed by means of the quantum mechanical package GAMESS on a five-node Pentium 4 cluster.[27] Basis sets used in the study included 6-31G(d,p)[28] for carbon, oxygen and hydrogen and SBKJC for bromine.[13] An initial guess for the atomic orbitals was performed by means of a Hückel estimation. Energy Hessian calculations were conducted at the end of each successful geometry optimization to determine the potential energy curvature in the vicinity of the minima found.

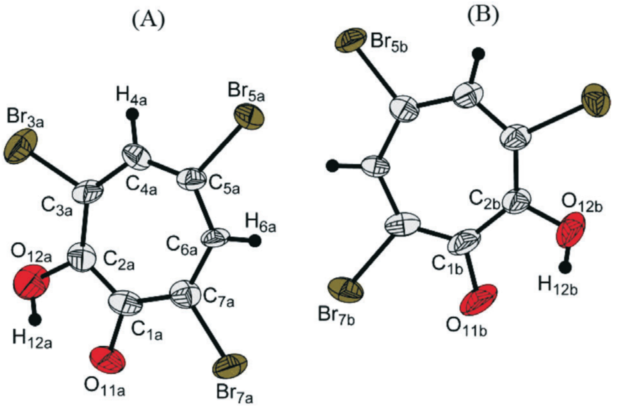

Figure 1 Diamond drawing of the $HTropBr_3$ (**A** and **B**) molecules in the asymmetric unit, showing the numbering scheme of the system.

3. Results and Discussion

3.1. X-ray Crystallography

The compound crystallized as neutral planar moieties in the monoclinic space group $P2_1$, with two independent molecules in the asymmetric unit. The numbering scheme of $HTropBr_3$ is presented in Fig. 1. The structure is twinned around the *b*-axis with a twin ratio of *ca.* 4:1, (twin matrix = [1 0 0; –1 0 0; 0 0 –1]). The merohedral twinning can be attributed in part to the short *a*-axis of 3.995(5) Å and elongated *b*- and *c*-axes, forming extended flat unit cells that can easily pack in a disordered mode in the solid state. On resolving the twin conformation of the system, a final R value of 6.35% was obtained. The most important bond distances and angles are reported in Table 2.

Although the two conformers A and B differ only slightly, both have unique intermolecular contacts with hydrogen bonding observed for the keto-enolate hydrogen. The tendency for troponoid type compounds to form extensive hydrogen bonding networks is known,[29] and in the case of 3,5,7-tribromotropolone the bromine atoms have replaced the oxygen donor atoms as possible hydrogen bonding sites (Fig. 2). Thus, the dimeric units are not observed as usually found in standard tropolone systems.[17] In both A and B bifurcated hydrogen bonding is observed for Br H-C (hydrogen interaction to three centres, *i.e.* Br_{5a}, O_{12a}, O_{11a}, with all three atoms lying in a plane with the hydrogen bond) (Table 3).

A bromine–bromine interaction is also observed, with a relatively short interatomic distance of the order of 3.8 Å. This type of interaction is not frequently observed, and is typically described in the literature as a weak interaction.[30] Since the van der Waals radius of bromine is 1.95 Å, the observed interaction in the solid state is quite strong, and is typically associated with the higher polarizability of the C-Br group.

Although the 5-nitrotropolone[17] ($HTropNO_2$) analogue also crystallized with two independent molecules in the asymmetric unit, the molecules differ only slightly, but exhibit the same inter- and intramolecular interactions in the unit cell. This is in contrast to the 3,5,7-tribromotropolone ($HTropBr_3$) compound described above, where the solid state interactions differ significantly from one conformer to another (Fig. 2).

3.2. Theoretical Study of Functionalized Tropolone Compounds

Owing to the different solid state interactions observed for the $HTropBr_3$, a systematic theoretical study was undertaken to evaluate these effects. The data reported in this section include the HTrop, $HTropBr_3$ and $HTropNO_2$ molecules (Table 4), and

Table 2 Selected bond distances and angles for $HTropBr_3$ (molecules A and B).

	A	B		A	B
			Bond length/Å		
O_{11}-C_1	1.326(18)	1.323(19)	C_4-C_5	1.390(20)	1.412(18)
O_{12}-C_2	1.313(17)	1.339(17)	C_5-C_6	1.385(19)	1.428(19)
C_7-C_1	1.400(20)	1.380(20)	C_6-C_7	1.457(19)	1.395(19)
C_1-C_2	1.430(20)	1.450(20)	C_3-Br_3	1.881(15)	1.933(15)
C_2-C_3	1.420(20)	1.390(20)	C_5-Br_5	1.912(14)	1.875(14)
C_3-C_4	1.398(19)	1.373(19)	C_7-Br_7	1.865(14)	1.888(14)
			Angle/°		
O_{11}-C_1-C_2	114.7(13)	113.8(14)	O_{11}-C_1-C_7	117.1(14)	119.4(16)
O_{12}-C_2-C_1	112.7(13)	114.5(13)	O_{11}-C_1-C_2	113.9(13)	114.5(14)
C_7-C_1-C_2-C_3	8(3)	–3(3)	C_3-C_4-C_5-C_6	–4(3)	–2(3)
O_{11}-C_1-C_2-O_{12}	–2(2)	1(3)	C_3-C_4-C_5-Br_5	180(1)	175(1)

the *cis*- or C_1 conformation as well as the *trans* rotamer and the transition state (C_{2v} or C_2) structures (Fig. 3). The study was conducted to determine the effect that functionalization of the tropolone core would have on the geometrical parameters as well as the electronic behaviour of the molecules. The general numbering scheme for the theoretical study is presented in Fig. 4.

The behaviour of the oxygen atoms, *i.e.* the keto-enolate structure, is of particular interest in each of the *cis* conformation systems under investigation. It is observed that the O–C distances are relatively unchanged in each system compared with the solid state structures and an ordering can only be made if the O…O distances are taken into consideration, *i.e.* $HTropNO_2$ > HTrop > $HTropBr_3$. This is due to the total effect of the keto-enol formation of the system, as well as the relative sensitivity of the O…O distances to electron-rich or electron-poor tropolone centres. The observed trend points to a restricted bonding mode in $HTropBr_3$ compared with the other systems under investigation (Table 4). This effect is further observed in the small change in the C_1–C_2 bond distances, following the same order as observed above.

It has been shown in previous papers that the *cis* configuration is favoured over the *trans* rotamer,[11,31] (*i.e.* 1a *vs.* 1c in Fig. 3), which is expected considering the stabilization induced by intramolecular hydrogen bonding to the keto oxygen atom. The relative similarity between the functionalized tropolones and the parent tropolone compound can be correlated with relative ease due to the minor computational expense[32] for each system involved.

The barrier height for the internal exchange of the proton in HTrop, $HTropNO_2$ and $HTropBr_3$ was investigated to determine if the electron-withdrawing substituents had any influence on the barrier height. The value for HTrop was expected to correlate with the previously reported value (MP2/6-31G(d)//HF/6-31G(d))[11] of 25.8 kJ mol^{-1}, and values calculated for $HTropNO_2$ and $HTropBr_3$ of 27.8 and 25.5 kJ mol^{-1}, respectively. The calculations were performed using both HF/6-31G(d,p) and MP2/6-31G(d,p) methodologies.[8,12] The effect of electron correlation significantly lowered the barrier height for HTrop from 53.3 to 12.6, $HTropNO_2$ from 50.4 to 14.3 and $HTropBr_3$ from 54.6 to 12.4 kJ mol^{-1}, respectively, for the HF to MP2 systems (Table 5). This is *ca.* 13 kJ mol^{-1} less than what has been reported previously for tropolone and it derivatives.[27] The change in energy can be attributed to the larger basis set as well as the method of optimization with electron correlation (MP2/6-31G(d,p)//MP2/6-31G(d,p)) included throughout the calculation.[33] It was thus observed that the effect of substitution is not as large as would have been suspected, but this can be attributed to the inherent

Table 3 Interaction distances observed for $HTropBr_3$.

Atom pair	Distance/Å	Atom pair	Distance/Å
H_{12A}…O_{11A}	1.944(13)	O_{11A}…H_{4A} (i)	2.972(17)
H_{12B}…O_{11B}	2.021(14)	Br_{7A}…Br_{3B} (ii)	3.794(3)
Br_{5A}…H_{6B}	3.205(8)	H_{4B}…O_{11B} (ii)	2.965(18)
H_{6A}…Br_{7B}	3.090(7)	H_{12B}…Br_{5B} (ii)	3.499(3)
H_{12A}…Br_{5A} (i)	2.964(2)	Br_{3A}…O_{12B} (ii)	3.163(11)

[Symmetry operators: (i) x, y – ½, –z + 2; (ii) x + 1, y + ½, –z + 1]

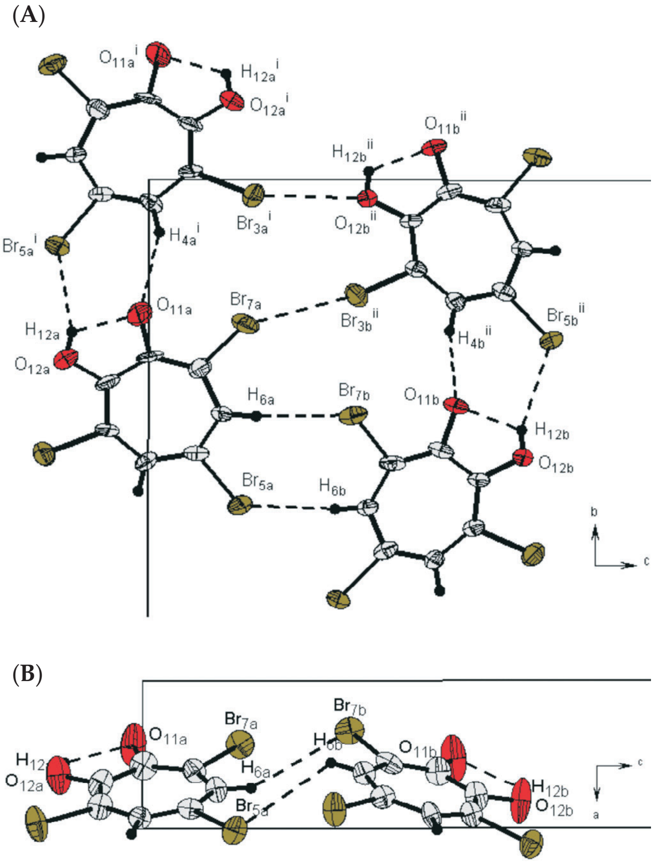

Figure 2 Partial unit cells for $HTropBr_3$ (**A** and **B**), viewed along the *a*-axis and the *b*-axis, with the most important inter- and intramolecular hydrogen bonding interactions indicated with dashed lines. Symmetry operators are given in Table 3.

Table 4 Selected bond distances and angles for HTrop, HTropNO$_2$ and HTropBr$_3$ compounds at the MP2/6-31G(d,p) level.

	HTrop			HTropBr$_3$			HTropNO$_2$		
	cis	C_{2V}	*trans*	*cis*	C_{2V}	*trans*	*cis*	C_{2V}	*trans*
O_{11}-C_1/Å	1.261	1.295	1.243	1.257	1.293	1.237	1.258	1.291	1.242
O_{12}-C_2/Å	1.340	1.295	1.356	1.335	1.293	1.349	1.335	1.291	1.352
O_{11}...O_{12}/Å	2.499	2.306	2.557	2.471	2.488	2.300	2.508	2.555	2.308
C_7-C_1/Å	1.437	1.405	1.457	1.447	1.410	1.472	1.440	1.406	1.461
C_1-C_2/Å	1.473	1.472	1.482	1.470	1.466	1.485	1.474	1.474	1.484
C_2-C_3/Å	1.382	1.405	1.378	1.389	1.410	1.384	1.383	1.406	1.378
C_3-C_4/Å	1.407	1.391	1.419	1.403	1.388	1.413	1.404	1.386	1.413
C_4-C_5/Å	1.382	1.398	1.373	1.381	1.394	1.371	1.376	1.395	1.367
C_5-C_6/Å	1.414	1.398	1.422	1.407	1.394	1.415	1.413	1.395	1.421
C_6-C_7/Å	1.377	1.391	1.370	1.376	1.389	1.370	1.372	1.386	1.365
O_{11}-C_1-C_2-O_{12}/°	0.000	0.000	0.000	0.000	0.000	0.000	0.230	–0.070	0.130
C_7-C_1-C_2-C_3/°	0.000	0.000	0.000	0.000	0.000	0.000	0.500	–0.500	0.630

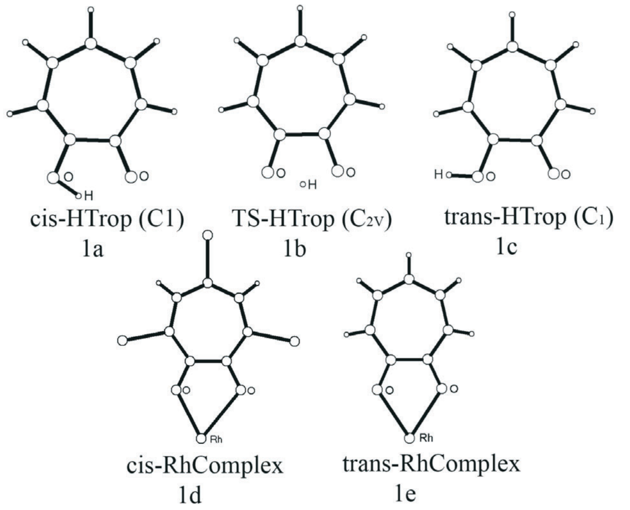

Figure 3 Diagrams of the rotamers of HTrop, *cis* (**1a**) and *trans* (**1c**), and the transition state C_{2v} (**1b**) with corresponding *cis* (**1d**) and transition state (**1e**) rhodium(I) complexes.

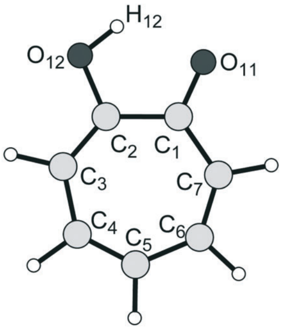

Figure 4 Diamond drawing of the calculated HTrop molecule, showing the numbering scheme of the system.

aromaticity of the tropolone core and the extent to which the oxygen atoms approach each other in the transition state (1b) (Table 4).

The low proton transfer barrier height for HTropBr$_3$ was somewhat surprising since the bromo moieties are expected to withdraw electron density from the tropolone core, due to the electronic properties of halogens, *i.e.* in that electron density is withdrawn *via* an inductive effect (electronegativity of the element) and the release of electron density by means of resonance in the aromatic system. This is predominantly observed in electrophilic aromatic substitution where halogens deactivate *ortho* and *para* directing groups. In the solid state this is balanced out by Br…Br interactions as well as hydrogen bonding sites (Fig. 2). Furthermore, the O…O distances for the HTropBr$_3$ decrease from 2.471 to 2.300 Å for the *cis* to C_{2v} configuration, compared with the solid state structure distances of 2.477 and 2.526 Å, which correlate well with the calculated ground state structure. For the transition state structure (C_{2v}) the trend is towards a more π-delocalized system on the troponoid ring. In the cases of HTrop and HTropNO$_2$ this tendency is continued, but the O…O distances have to contract over a larger distance, which in turn creates more strain in the respective molecules (Table 5). Furthermore, the change for HTropBr$_3$ in the C–O bond distances, from 1.257 and 1.335 Å to 1.293 Å, during proton transfer is less than that observed for HTrop and HTropNO$_2$. This contributes to the lowering of the energy barrier height, as well as the stabilizing effect on the system by the bromine moiety

Table 5 Energy values for RHF/6-31G(d,p) and MP2/6-31G(d,p), and ΔE values.

		Energy/*H*			ΔE/kJ mol^{-1}
		RHF	MP2	ZPE	
HTrop	C_1	–418.27322	–419.54696	0.11619	0
	TS (C_{2V})	–418.24824	–419.5385	0.11252	12.6
	trans	–418.25692	–419.52647	0.11546	51.9
HTropNO$_2$	C_1	–621.73982	–623.54477	0.11845	0
	TS (C_2)	–621.71595	–623.53555	0.11467	14.3
	trans	–621.72396	–623.52539	0.1178	49.2
HTropBr$_3$	C_1	–455.89198	–457.25382	0.08493	0
	TS (C_{2V})	–455.86634	–457.2456	0.08142	12.4
	trans	–455.88002	–457.23624	0.08433	44.6

Table 6 Selected Mulliken charges and dipole moments for the tropolone molecules.

	HTrop			$HTropNO_2$			$HTropBr_3$		
	cis	*trans*	C_{2v}	*cis*	*trans*	C_2	*cis*	*trans*	C_{2v}
O_{11}/e	–0.540	–0.459	–0.567	–0.517	–0.439	–0.547	–0.505	–0.412	–0.536
O_{12}/e	–0.537	–0.509	–0.567	–0.521	–0.495	–0.547	–0.510	–0.486	–0.536
H_{12}/e	0.362	0.336	0.410	0.368	0.343	0.416	0.372	0.335	0.419
μD^a	3.619	4.971	4.127	1.170	3.226	0.569	2.375	3.802	2.900

$^a 1\ D = 3.336 \times 10^{-30}$ C m.

adjacent to the hydrogen atom, forming a partial hydrogen bonding environment.

Although Mulliken charges are of relative use, it is clear that the order of charge localization for O_{11} and O_{12} is HTrop > $HTropNO_2$ > $HTropBr_3$ (Table 6). This is due to the aromatic nature of the ring, with the parent compound HTrop having a better delocalized π-system than $HTropNO_2$ or $HTropBr_3$. In the case of $HTropNO_2$, the nitro group can contribute to the delocalization of π-electrons in the system but polarizes the troponoid moiety into two electronegative centres (nitro and keto-enol moieties). This is clearly observed in the dipole moments of the associated troponoid systems (Table 6), with the same basic trend followed by the Mulliken analysis. It is interesting to note that the predicted dipole moment for $HTropNO_2$ of $\mu < 1$ D[34] is nearly reproduced in MP2/6-31G(d,p)[11] calculations ($\mu = 1.1702$ D (*cis*) and 0.5693 D (C_2); $1\ D = 3.336 \times 10^{-30}$ C m). In addition to this, the effect of the bromine moieties on the charge localization on the proton in the *cis vs. trans* isomers is clearly observed by the relatively small difference in charge for $HTropBr_3$, which is similar to HTrop (Table 6). The preference for proton transfer in the case of $HTropBr_3$ should be higher, due to the charge delocalization over the troponoid ring system, as observed in the Mulliken charges on the oxygen atoms as well as the relative rigidity of the tropolone core system during formation of the transition state.

The observed trend is continued in *cis-trans* conformations of the different tropolone systems, *i.e.* $HTropBr_3$ has the minimum energy change with conformation of the tropolone systems under investigation (HTrop 51.9, $HTropNO_2$ 49.2 and $HTropBr_3$ 44.6 kJ mol^{-1}) as well as a relatively small change in distances and angles in the tropolone core. A further reason for the stability of the *trans* isomer of $HTropBr_3$ is the close proximity of the bromo moiety to the proton.

The relative rigidity of the $HTropBr_3$ core might explain why the solid state behaviour of the system is so unique for both HTrop and $HTropNO_2$, which form dimeric structures in the unit cell, *i.e.* the hydrogen bonding networks between the oxygen atoms (O_{11} and O_{12}) balance out excess electron density. In the case of $HTropBr_3$ this is absent, due to the decrease of electron density on the oxygen atoms as well as the availability of better hydrogen bonding sites in the bromine moieties.

3.3. Comparison with Transition Metal Tropolonato Complexes

In a coordinated state, the tropolonato ligand will tend to delocalize the π-electron density over the seven-membered aromatic carbon ring backbone, creating symmetry equivalent bond distances and angles due to enolization of the keto group. A select group of transition metal complexes ([Rh(TropY)(CO)(XZ_3)]; TropY = Trop, $TropBr_3$, $TropNO_2$; XZ_3 = tertiary group 15 ligands, *i.e.* X = P, As; Z = Ph_3, $FcPh_2$) were chosen to evaluate the effect of coordination on the structural parameters of tropolonato ligands (Table 7) (the first three entries refer to the uncoordinated ligand in the solid state).

The parent compound, HTrop, gives a general description of the behaviour of the bidentate mode of bonding to the rhodium(I) metal centre. The hydroxyl (O_{12}–C_2) moiety bond distance decreases, while the carbonyl (O_{11}–C_1) moiety increases

Table 7 Selected crystallographic data of tropolone compounds and rhodium(I) mono and bis-phosphine complexes containing a carbonyl moiety.

Compound	O_{11}-C_1 /Å	O_{12}-C_2 /Å	C_{11}-C_{12} /Å	O_{11}-C_1-C_2-O_{12} /°	C_7-C_1-C_2-C_3 /°	$O_{11}…O_{12}$ /Å	O_{11}-Rh /Å	O_{12}-Rh /Å	O_{11}-Rh-O_{12} /°
HTrop$^{(a)}$	1.33(3)	1.26(4)	1.45(4)	1.61(7)	1.96(4)	2.55(2)			
	1.327(2)	1.241(2)	1.478(2)	2.6(2)	3.6(3)	2.56(2)			
$HTropNO_2^{(b)}$	1.332(2)	1.246(2)	1.474(2)	0.7(2)	1.2(3)	2.54(4)			
	1.32(2)	1.31(2)	1.43(2)	–2(2)	8(3)	2.5(2)			
$HTropBr_3^{(TW)}$	1.32(2)	1.34(2)	1.45(2)	1(3)	–3(3)	2.5(3)			
$[Rh(Trop)(CO)_2]^{(c)}$	1.267(9)	1.324(8)	1.47(1)	–1(1)	–4(1)	2.589(8)	2.032(5)	2.021(5)	79.4(2)
$[Rh(Trop)(CO)(PPh_3)]^{(d)}$	1.30(8)	1.29(9)	1.46(10)	–1(2)	–2(9)	2.58(6)	2.03(5)	2.08(9)	77.8(6)
$[Rh(Trop)(CO)(AsPh_3)]^{(e)}$	1.31(1)	1.27(1)	1.47(1)	–3(1)	–10(2)	2.58(2)	2.039(6)	2.059(6)	78.1(2)
$[Rh(Trop)(CO)(PFcPh_2)]^{(f)}$	1.295(3)	1.281(3)	1.449(3)	–0.1(3)	–2.28(4)	2.588(2)	2.049(1)	2.084(1)	77.56(6)
$[Rh(TropNO_2)(CO)(PPh_3)]^{(g)}$	1.274(7)	1.275(6)	1.477(8)	1.5(7)	3.2(9)	2.574(6)	2.068(4)	2.072(4)	77.1(2)
$[Rh(TropBr_3)(CO)(P(Obtbp)_3)]^{(h)}$	1.299(6)	1.277(6)	1.474(8)	0.9(8)	0.0(1)	2.579(5)	2.036(4)	2.064(4)	78.0(2)
$[Rh(Trop)(CO)(PFcPh_2)_2]^{(i)}$	1.268(3)	1.268(3)	1.468(6)	12.93(4)	20.5(4)	2.60(3)	2.302(2)	2.302(2)	68.9(1)
$[Rh(TropBr_3)(CO)(PPh_3)_2]^{(i)}$	1.264(6)	1.265(7)	1.463(9)	1.9(9)	9.5(1)	2.568(6)	2.161(4)	2.485(4)	66.7(2)
$[Rh(TropBr_3)(CO)(AsPh_3)_2]^{(i)}$	1.29(3)	1.25(3)	1.47(3)	–2.3(3)	–9.6(3)	2.575(2)	2.166(5)	2.464(6)	66.8(2)

(TW) This work, (a) H. Shimanouchi, Y. Sasada, *Acta Cryst.*, B29, 1973, 81, (b) K. Kubo, E. Yamamoto, A. Mori, *Acta Cryst.*, C57, 2001, 611, (c) G. Steyl, G.J. Kruger, A. Roodt, *Acta Cryst.*, C60, 2004, m473, (d) J.G. Leipoldt, L.D.C. Bok, S.S. Basson, H. Meyer, *Inorg. Chim. Acta*, 42, 1980, 105, (e) G. Steyl, A. Roodt, *Acta Cryst.*, E, 2005, in press, (f) G. Steyl, S. Otto, A. Roodt, *Acta Cryst.*, E57, 2001, m352, (g) G. Steyl, A. Roodt, *Acta Cryst.*, C60, 2004, m324, (h) R. Crous, M. Datt, D. Foster, L. Bennie, C. Steenkamp, J. Huyser, L. Kirsten, G. Steyl, A. Roodt, *J. Chem. Soc., Dalton Trans.*, 2005, 1108, (i) A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.*, 245, 2003, 121.

due to bond formation and delocalization of the π-electron density through the tropolonato moiety (Table 7). Furthermore, the C_{11}–C_{12} bond distance remains unchanged by the variation of both substituents on the tropolone ring or coordination to the rhodium(I) metal centre. In contrast to this, the variation in torsion angles of the carbonyl moieties (O_{11}-C_1-C_2-O_{12}) is observed for the bis-ferrocenyldiphenylphosphine ($PFcPh_2$) complex. The observed distortion can be attributed to both the electron-rich donating phosphine ($PFcPh_2$) ligands as well as the packing methodology in the solid state. The flexibility of the tropolonato ring system is further apparent from the torsion angle variation of the seven membered carbon ring (C_7-C_1-C_2-C_3), although the $HTropBr_3$ derivatives have smaller torsion angles.

The coordination mode of the tropolonato ligands in the mono-phosphine rhodium(I) complexes is nearly equivalent, as observed from Table 7. This bonding conformation changes significantly for the bis-phosphine/arsine complexes, *i.e.* the parent compound (HTrop) having equivalent Rh–O bond distances compared with the unsymmetrical bonding mode for the bromo derivative ($HTropBr_3$) complexes. The Rh-O bond distortion induces a conformational change from trigonal pyramidal to square planar pyramidal, effectively decreasing the bite angle (O-Rh-O) (Table 7). This conformational change can be attributed to the rigidity of the $HTropBr_3$ ligand as well as the weak electron-donating ability of this compound.

4. Conclusion

The orientation of the hydroxyl hydrogen on the tropolone moiety has been discussed in detail in the current study and an energy minimum has been identified in the classical hydrogen bonded *cis*-conformation (Fig. 3 and Table 5). The *trans*-conformation lies at a higher energy plateau, with a possible hydrogen interaction observed for the trans-$HTropBr_3$ rotamer. Thus the inclusion of bromo groups in the tropolone system stabilizes the different conformational rotamers due to both the electron donating and withdrawing ability of the halogen moieties.

The Br…Br distances observed for $HTropBr_3$ and $HHinBr_2$[35] ligands tend to be ~3.6 to 3.8 Å. Hence, these solid state interactions are relatively strong and tend to have a stabilizing effect on the crystallization modes of these compounds. Furthermore, two different interactions were observed for the compounds since $HHinBr_2$ has a Br-π interaction with the delocalized tropolonato system and the $TropBr_3$ compound forms hydrogen bonds with the hydroxyl group of the associated tropolone system.

An overlay of the calculated and solid state structures observed for the tropolone compounds, indicate an excellent correlation (Fig. 5). Both the solid state $HTropBr_3$ structures have an RMS[36] overlay of 0.0776 Å and 0.0908 Å, indicating a similarity to the calculated structure although both the independent molecules differ in bonding orientation. The overlay of the $HTropNO_2$ and HTrop compounds has an RMS value of 0.1556 Å and 0.0678 Å, respectively. Although $HTropNO_2$ has two independent molecules in the unit cell, the molecular conformation does not differ significantly, as observed from the RMS value. The small deviation of the RMS value can be ascribed to the rotation of the nitro moiety.

The effect of the tropolonato moiety on the solid state character of the title compounds has been investigated in conjunction with different functional groups. The use of theoretical methods to extend the study into the effects of functionalization on the tropolone moiety have been successfully incorporated to determine polarity and preferred energy conformations of the tropolone systems.

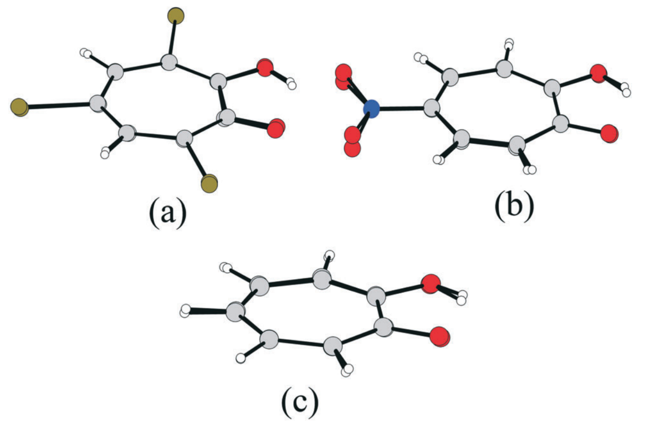

Figure 5 RMS overlay figures of the calculated (MP2) and solid state structures of $HTropBr_3$ (**a**), $HTropNO_2$ (**b**) and HTrop (**c**) compounds. Overlay fit includes all atoms in the tropolone moieties.

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