Molecular Mechanics (MM3*) Parameters for Ruthenium(II)−Polypyridyl Complexes

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We have developed molecular mechanics parameters for Ru^{II}−polypyridyl coordination compounds with the MM3* force field in MacroModel. X-ray structures, together with a B3LYP frequency calculation on a model system, have been utilized in the parametrization. The performance of the force field and the quality of each parameter is analyzed. A clear qualitative correlation have been found between coordination geometry and emission properties for the ruthenium polypyridyl complexes examined in this paper.

Introduction

Ever since the first report[1] of the light-emitting properties of the photoexcited state of $[Ru(bpy)_3]^{2+}$, intense research efforts have been directed toward increasing the understanding of the photophysical and photochemical properties of Ru^{II}−polypyridyl complexes. These have found frequent use as photosensitizers and photoelectron donors, due to a unique combination of chemical stability and favorable redox and excited-state properties.[2] In addition, the polypyridine ligands (bipyridine, phenanthroline, terpyridine, etc.) can be synthetically modified using the tools of organic chemistry, thus allowing extensive possibilities for structural variations.[3] More complex systems have been studied as model systems for artificial photosynthesis,[4] such as bi- or polynuclear Ru^{II}−Ru^{II} [5] or Ru^{II}−Os^{II},[6] and bi- and polynuclear complexes containing a range of transition metals including Ru^{II} and Os^{II}.[2b] Other examples include systems displaying an even higher level of organization, such as donor−sensitizer−acceptor arrays,[7] membrane-bound,[8] intrazeolitic,[9] polymeric,[10] DNA-intercalating,[11] or interacting with monoclonal antibodies.[12] There have also been successful attempts to synthesize (rather than resolve by crystallization) enantiometrically pure Ru^{II}−polypyridine complexes.[13]

The important photophysical properties of excited-state lifetime (τ), quantum yield of formation (ϕ), and redox potential are intimately tied to the molecular architecture. The ligand identity, the substitution pattern on the ligand, the steric requirements and the identity of the bond-forming atom (most frequently nitrogen, but complexes containing Ru−O and Ru−P bonds are known) are all important factors. Also, the overall coordination geometry, which is more or less ideally octahedral, seems to have a crucial influence on these properties; the final result being a composite of these above factors. One very attractive use of structure calculation methods is to employ these as a tool, to further the understanding of the nature of the geometrical requirements of a "good" emitting state. We have earlier sought to quantify the relation between the complex

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geometry and the emission properties for a series of ruthenium complexes composed of ligands with varying steric bulk,[14] and in complexes possessing Ru−N and Ru−O bonds.[15] The correlations between structure and photophysical properties are not easy to extract from the literature. These properties are frequently *not* reported in the same piece of work, partially reflecting the fact that different molecular properties lead to either successful crystallization, or interesting photophysical properties; and further the different research objectives of our fellow scientists. A systematic application of a sound computational method might allow a comparison between a much larger set of complexes, by inferring reasonably accurate solution structures, which hopefully could be correlated to the photophysical and photoelectron-transfer properties. The development of a successful theoretical model for the correlation of ligand−ruthenium interaction in relation to the predicted (or determined) complex geometry thus could afford guidance in the design and synthesis of novel complexes with improved photophysical properties.

The molecular mechanics parameter set developed in this work could also be applied to supramolecular systems with torsional flexibility or in systems composed of more than one molecule, for example DNA intercalation of ruthenium complexes. In this area the need for molecular mechanics is urgent, since the interpretation of the photophysics in these systems is highly dependent on the possibility to understand the conformational behavior of the molecule or the intermolecular interactions. A conformational search could provide valuable information about distances between Ru^{II} and primary acceptors or donors. A molecular mechanics treatment could also supply information on factors influencing conformational preferences.

Theoretical approaches to the molecular structure of ruthenium polypyridyls have earlier been made on a semiempirical basis. Recently, ruthenium parameters were released for use in the PM3 method implemented in the Spartan program package.[16] This parameter set has been examined briefly in this work. An attempt to cover both the geometrical and the photophysical behavior of this class of photosensitizers as well as other ruthenium complexes has been described by Broo et al.,[17] using the semiempirical method INDO.

Semiempirical methods are very fast compared to high level quantum chemical methods. Geometry optimization of medium-size complexes are feasible, but extensive conformational searching of flexible ligands will probably be outside the computational resources of most researchers soon. The accuracy in conformational energies is also limited to at best ca. 5−10 kJ/mol.[18] A good alternative is using force field methods (molecular mechanics).[19] These are several magnitudes faster even than semiempirical methods and, with carefully chosen parameters, an accuracy of ca. 2 kJ/mol is achievable for conformational energy differences.[18] Most current molecular mechanics programs were designed primarily for purely organic compounds. Metal-containing systems are notoriously difficult to describe in terms of the standard functions employed in classical force fields.[20] Many of the problems arise from the treatment of bond angles, which can have multiple and widely varying values in metal complexes. However, the current system is unusually well suited for force field parametrization, as the coordination is well described by a quite rigid octahedron. This type of coordination is easily treated by the tools in the MacroModel package.[21] In this work we have chosen to work with the MM3* force field. MM3* is one of the most accurate force fields currently available,[18] the parameters are easily modified using a newly developed parameter optimization method,[22] and the functional form is designed to reproduce vibrational spectra.[23] The latter is especially important, as we have used quantum chemical Hessian information in the parametrization and plan to utilize the force field for elucidation of vibrational spectra.

Preparation of Input Data

X-ray Structural Data. Structures were extracted from the Cambridge Crystallographic Data Base (CCDB),[24] excluding all structures with $R \geq 8\%$. A total of 27 structures of 16 different types were selected (Figure 1).[25] All bond distances,

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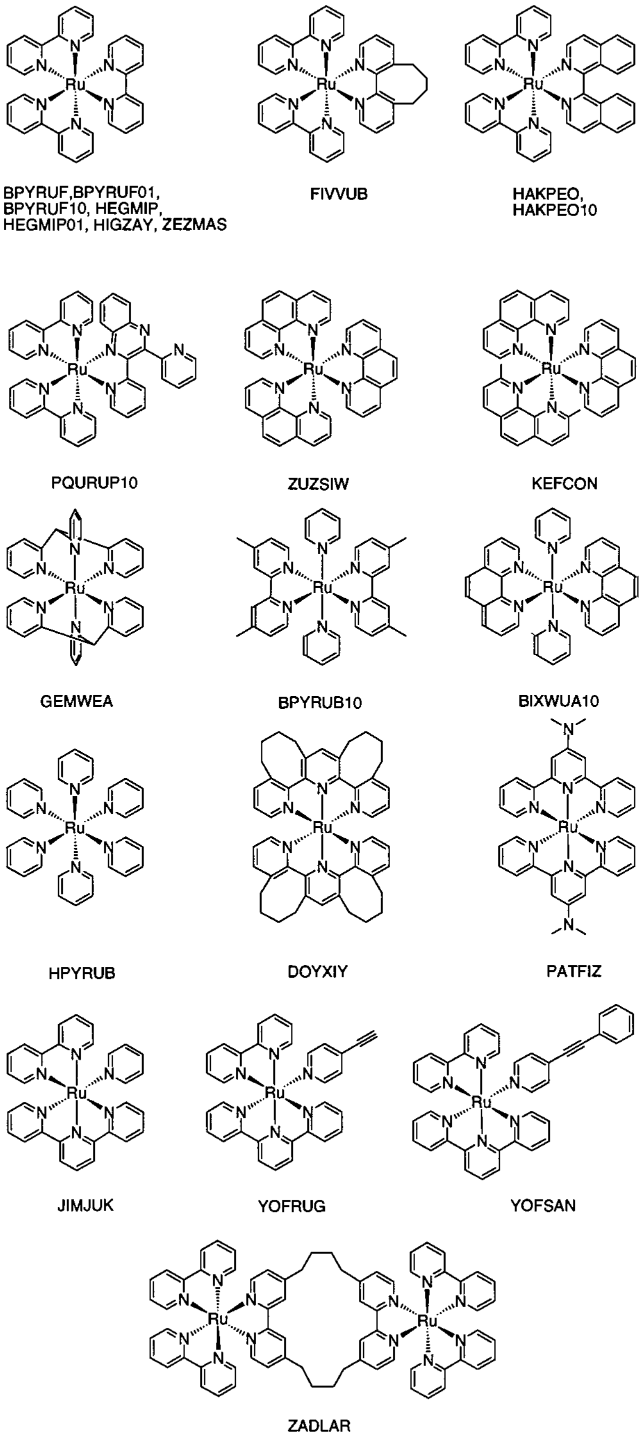

Figure 1. X-ray structures used in the parametrization.

bond angles, and torsional angles for which parameters were refined and that did not incorporate hydrogens were used as reference data in the parametrization, yielding a total of 3959 data points.

Quantum Mechanical Calculations. To improve the atomic charges and the force constants, a quantum mechanical calculation was made on a small model system. As a model for Ru^{II}–polypyridine type complexes we have chosen Ru^{II}tris(glyoxaldiimine) (**1**, Figure 2).

Calculations were performed using the Gaussian94 program.[26] The B3LYP hybrid functional[27] was employed together with the 6-31G* basis set for all atoms except ruthenium. A suitable ECP basis of TZV quality was obtained for ruthenium by splitting off the most diffuse s, p, and d primitive in the standard LANL2DZ contraction.[28] The geometry was fully optimized in D_3 symmetry, whereupon the Hessian was calculated numerically, yielding a total of 2850 unique mass-weighted Hessian elements, which were used as reference data in the parametrization. The Hessian was used without scaling.[29] CHelpG charges[30] were calculated using a radius of 2.34 Å for ruthenium.[31]

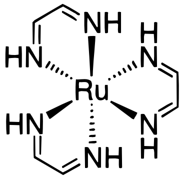

Figure 2. Ru^{II}tris(glyoxaldiimine).

PM3(tm) calculations on selected complexes from Figure 1 were performed in the Spartan program.[16]

Molecular Mechanics Calculations. All force field calculations were performed on Silicon Graphics workstations utilizing MM3* in MacroModel V6.0,[21] using default settings consistently. The MM3* force field is based upon, but not identical to the 1989 version of the Allinger MM3 force field.[23] The parameters are usually interchangeable, but some differences in paradigm should be noted. The electrostatics in MM3 is based mainly upon dipole interactions (but also includes charge–charge and charge–dipole interactions), whereas MM3* utilizes point charges determined by using the MM3 dipoles as charge flux parameters. MM3* also uses a nondirectional 10-12 Lennard-Jones-type potential for hydrogen bonds in lieu of the directional Buckingham potential in MM3. For conjugated systems, MM3 uses a VESCF scheme to determine π-bond orders, and scales bond and torsional parameters according to the calculated bond order. MM3* instead relies on user identification of single or double bonds and uses a substructure matching scheme to identify and reparametrize specific conjugated systems.

Description of the Substructure and Choice of Bonding Model. There are several options for how to model the bonding between metal and ligands in molecular mechanics force fields.[20] The simplest is to treat the metal as a free atom/ion, using solely nonbonded interactions to determine the geometry. The next step is to introduce a metal–ligand bond but to describe all ligand–ligand interactions by nonbonded interactions (this is sometimes called the points-on-a-sphere, or POS, model). Finally, in the valence bond model the entire complex is treated as a covalently bound entity, using standard stretching, bending, and torsional potentials to describe intramolecular interactions. The valence bond model, which has been used in the current

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Table 1. Weighting Factors Used in Merit Function Calculation

data type	w
bond length	100 Å^{-1}
bond angle	2 deg^{-1}
torsion angle	1 deg^{-1}
mass-weighted Hessian element	0.1 kJ^{-1} mol Å^2 amu^{-1}

work, requires further choices regarding which angle bending terms should be utilized. In the simple case of an octahedral geometry, the bending potential should have two minima, close to 90 and 180°. An elegant approach is to utilize a periodic functional form with multiple minima.[32] However, this type of functional form is not available in the current version of MacroModel. We have instead implemented a substructure identification of ligands in a cis or trans relationship, each interaction with it's own set of parameters. The trans angle reference value was kept at 180° to avoid creating a singularity (a cusp). Note that the identification and parameter assignment is based on the starting geometry. This avoids creating a cusp at the crossover point (ligands cannot switch between a cis and trans relationship during minimization) but requires the starting geometry to be reasonably octahedral.

All stretching, bending, and torsional parameters incorporating ruthenium were subjected to optimization. The ruthenium van der Waals parameters were taken from Allinger et al.,[31] and used without further refinement. The formal charge of ruthenium was set to +2 to reproduce the overall charge of the complexes. The dipoles (or more properly, charge flux parameters) of the Ru–N and N–C bonds were adjusted to reproduce as closely as possible the calculated CHELPG charges of **1** and then kept fixed. Due to the high symmetry of the octahedral center, only a 4-fold (v_4) term was used for the torsion around the Ru–N bond (N–Ru–N–C). The availability of quantum chemical Hessian information allowed inclusion of the N–Ru–N stretch–bend term in the parametrization. Of already existing parameters in the MM3* force field, only the out of plane parameter for N_{sp^2} and the stretching parameters for the bond between carbon and the coordinated nitrogen were refined further.

It was noted that in particular monoterpyridine complexes display a geometric trans influence that could not be fully reproduced by the optimized force field. It was found necessary to incorporate a term that elongates a Ru–N bond when the trans bond is compressed. Intuitively, this should be viewed as a stretch–stretch interaction, but Macromodel does not include this feature. We settled instead for a direct "bonding" interaction added by the substructure for all ligands in a trans relationship. The only effect of this nonphysical "bond" is to keep the trans N–N distance fairly constant. The parameters of this added "bond" were included in a complete reoptimization of the entire force field. The two final force fields are designated "trans" and "notrans".

Parametrization Method. The parametrization was performed according to the new method developed by Norrby and Liljefors.[22] A *merit function* for the force field was defined as a weighted squared sum of deviations from the reference values. The weighting factors employed are defined in Table 1. The merit function was minimized by variation of the parameters, using numerical Newton–Raphson techniques.[22] The convergence criteria were (1) no further improvement should be obtained by any modified Newton–Raphson step and (2) the second derivative of the merit function with respect to each parameter must be positive and large compared to the corresponding first derivative.

Table 2. Bond Parameters: k_s (Mdyn/Å), l_0 (Å), Bond Moment (D)

	notrans		trans		bond
atom types	k_s	l_0	k_s	l_0	moment
N_{sp^2}–Ru	2.6837 ±0.057	2.0812 ±0.0008	1.473 ±0.047	2.0811 ±0.0011	2.6941[a]
N_{sp^2}–C_{sp^2}	6.6089 ±0.081	1.3384 ±0.0010	6.748 ±0.093	1.3344 ±0.0013	−1.9191[a]
N_{sp^2}–H	6.4644 ±0.043	1.0285 ±0.0009	6.453 ±0.043	1.0286 ±0.0009	−1.6442[a]
N_{sp^2}···N_{sp^2}(trans)	–	–	0.636 ±0.065	4.1270 ±0.0012	–

[a] Internally used as charge flux parameters, set to reproduce CHELPG charges, not refined. In a typical complex (e.g., $[Ru(bpy)_3]^{2+}$) the bond moments shown result in point charges of +0.383 on Ru and −0.328 on N.

Table 3. Angle Parameters: k_b (mdyn Å/rad^2) and θ_0 (deg)

	notrans		trans	
atom types	k_b	θ_0	k_b	θ_0
N_{sp^2}–Ru–N_{sp^2} (cis)	0.5638 ±0.0042	91.0907 ±0.11	0.5990± 0.0056	93.10± 0.16
N_{sp^2}–Ru–N_{sp^2} (trans)	0.1760 ±0.013	180[a]	0.205 ±0.013	180[a]
C_{sp^2}–N_{sp^2}–Ru	0.7195 ±0.0050	123.5054 ±0.12	0.7281 ±0.0059	125.38 ±0.18
Ru–N_{sp^2}–H	0.0578 ±0.022	143.7801 ±5.6	0.044 ±0.017	151.1 ±5.7

[a] Not refined.

Table 4. Torsional Parameters v (kcal/mol)

atom types	type	notrans	trans
Ru–N_{sp^2}–C_{sp^2}–C_{sp^2}	v_1	−2.8131 ± 0.065	−5.037 ± 0.070
	v_2	2.4143 ± 0.048	2.509 ± 0.063
Ru–N_{sp^2}–C_{sp^2}–C_{sp^3}	v_2	−0.75 ± 0.5	−0.75 ± 1.0
N_{sp^2}–Ru–N_{sp^2}–C_{sp^2}[a]	v_4	−0.2508 ± 0.0060	−0.2818 ± 0.0055
Ru–N_{sp^2}–C_{sp^2}–H	v_2	10.538 ± 0.082	10.762 ± 0.056

[a] Set to zero when N–Ru–N is identified as trans.

Table 5. Other Parameters

type	central atom	notrans	trans
van der Waals ϵ (kcal/mol)	Ru	0.438[a]	
van der Waals r (Å)	Ru	2.34[a]	
stretch-bend k (mdyn/rad)	Ru	0.0351 ± 0.005	0.089 ± 0.010
out-of-plane k (mdyn Å/rad^2)	N_{sp^2}	0.0595 ± 0.0027	0.0561 ± 0.0027

[a] From ref 31, not refined.

Results

Optimized Parameters. The optimized parameters are presented in Table 2–5. For each parameter, the optimal value and a calculated range are shown. The latter is the change in the parameter needed to increase the merit function by 0.1%, corresponding to for example an increased rms error in Ru–N bond length of 0.004 Å (a value that is certainly measurable but not very significant to the overall performance of the force field). The range is calculated from the second derivative of the merit function with respect to the parameter,[22] determined by central numerical differentiation. Note that the ranges corre-

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(32) (a) Allured, V. S.; Kelly, C.; Landis, C. R. *J. Am. Chem. Soc.* **1991**, *113*, 1. (b) Cleveland, T.; Landis, C. R. *J. Am. Chem. Soc.* **1996**, *118*, 6020.

Table 6. Deviation between Calculated and Observed Values, in Å or Deg, Respectively

	notrans			trans			PM3(tm)[a]		
	rms[b]	ME[c]	MaxAE[d]	rms	ME	MaxAE	rms	ME	MaxAE
Ru−N_{sp^2}	0.01	−0.001	0.054	0.01	−0.002	0.038	0.01	0.005	0.041
(Ru-)N_{sp^2}−C_{sp^2}	0.01	−0.005	0.054	0.01	−0.003	0.052	0.04	−0.038	0.084
N_{sp^2}•••N_{sp^2} (trans)	0.02	−0.003	0.067	0.02	−0.005	0.062	0.02	0.010	0.053
N_{sp^2}•••N_{sp^2} (cis)	0.04	−0.001	0.182	0.04	−0.002	0.181	0.06	0.007	0.133
N_{sp^2}−Ru−N_{sp^2} (trans)	1.65	−0.481	6.416	1.64	−0.481	6.463	1.96	−0.365	6.453
N_{sp^2}−Ru−N_{sp^2} (cis)	1.67	0.018	6.345	1.67	0.014	6.324	2.32	0.000	5.348
C_{sp^2}−N_{sp^2}−Ru	1.12	−0.323	3.691	1.08	−0.297	3.704	2.08	−1.574	4.857
Ru−N_{sp^2}−C_{sp^2}- C_{sp^2}	5.76	−0.183	14.800	5.76	−0.179	15.200	4.84	−0.001	11.600
Ru−N_{sp^2}−C_{sp^2}−C_{sp^3}	2.63	0.225	4.800	2.63	0.238	4.800	6.92	−0.592	27.200
N_{sp^2}−Ru−N_{sp^2}−C_{sp^2}	4.55	−0.264	15.000	4.53	−0.266	14.700	7.35	−0.811	24.200
N_{sp^2}OOP	4.81	−0.154	14.400	4.78	−0.147	13.200			

[a] A selection of complexes have been used in this evaluation, these are BIXWUA10, DOYXIY, HAKPEO, HPYRUB, JIMJUK, and PATFIZ. [b] Root-mean-square error. [c] Mean error. [d] Maximum absolute error.

Table 7. Energy Excess[a] (kJ/mol)

		no trans parameter included		trans parameter included		
x-ray structure	*R*	frozen[b]	constrained[c]	frozen[b]	constrained[c]	PM3(tm)[b]
BIXWUA10	0.0470	67	17	69	19	147
BPYRUB10	0.0470	35	16	38	17	
BPYRUF	0.0440	64	20	64	20	
BPYRUF01	0.0270	32	18	33	18	
BPYRUF10	0.0440	63	20	64	20	
ZUZSIW	0.0435	79	18	79	19	
DOYXIY	0.0650	160	57	164	62	248
FIVVUB	0.0580	146	44	148	44	
GEMWEA	0.0500	32	12	31	11	
HAKPEO	0.0530	68	18	70	19	124
HAKPEO10	0.0530	67	18	69	19	
HEGMIP	0.0340	41	23	42	23	
HEGMIP01	0.0370	38	22	39	22	
HIGZAY	0.0350	88	38	88	38	
HIGZAY	0.0350	104	36	106	36	
HPYRUB	0.0630	89	27	91	29	192
JIMJUK	0.0550	66	28	64	29	155
KEFCON	0.0740	191	30	192	31	
ZADLAR	0.0420	237	209	240	212	
PATFIZ	0.0667	93	40	96	42	185
ZEZMAS	0.0450	40	15	40	15	
PQURUP10	0.0672	95	39	98	40	
YOFRUG	0.0427	89	21	84	21	
YOFSAN	0.0456	123	39	121	39	

[a] The energy excess is defined as the energy difference between the fully optimized structures and the related X-ray structures. The hydrogens were fully relaxed in all optimizations. [b] Heavy atoms were frozen in the relaxation. [c] Heavy atoms were restrained using a harmonic penalty function of 500 kJ/mol Å^{-2} in the relaxation.

spond to single parameter changes. In many cases, two or more parameters can be varied together without significantly changing the merit function. These cases can be identified by examining low eigenvalues of the parametrization design matrix.[22]

Parameters including the N−H moiety were included only to enable use of the quantum mechanical Hessian in the parametrization. No experimental structures including this moiety were included in the parametrization. However, the parameters for the N−H moiety are not needed for the main target molecules (Figure 1), and their quality was therefore considered unimportant.

Performance of the Force Field in Geometry Determinations. The performance of the force field with respect to determinations of geometries have been evaluated by comparing the optimized structures by the structures reported from X-ray determinations. This was done by analyzing the bond lengths, angles, and dihedrals separately. The results are presented in Table 6.

Performance of the Force Field in Energy Determinations. The differences in energy between X-ray structures and minimized structures have been determined and are presented in Table 7. This energy, entitled the energy excess, is defined as the energy difference between a relaxed X-ray structure and the corresponding fully optimized global minimum for the structure. In the relaxation, all hydrogens were allowed to find their optimum positions, whereas the heavier atoms were either completely fixed (in Macromodel: "frozen") or restrained with a harmonic tethering potential ("fixed" in MacroModel vocabulary). As all X-ray structures contain small errors and all are subject to crystal packing forces, even an ideal force field will give a positive excess energy for all structures. However, for an optimal force field, the energy excess of all well-determined X-ray structures should be low. The energy excesses have also been evaluated by the PM3(tm) method (Table 7). This method gives considerably higher energies than MM3*.

Second Energy Derivatives: Hessian Matrix Elements. The correlation between mass-weighted energy second derivatives calculated by the molecular mechanics force field and by quantum chemistry have been determined. Also, the correlation between PM3(tm) and B3LYP have been evaluated. The results are represented in Figure 3 and Table 8.

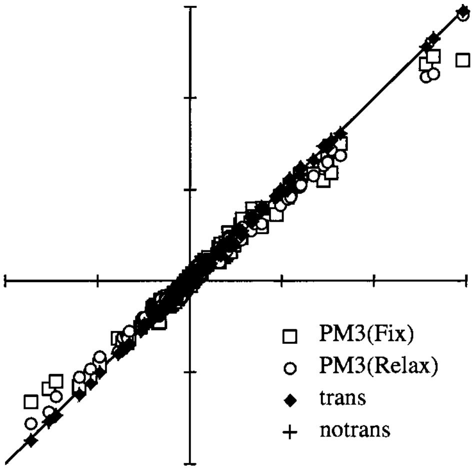

Figure 3. Plot of the Hessian matrix elements. Molecular mechanics (trans and notrans) and PM3(tm) vs B3LYP. The PM3(Fix) values have been derived using the B3LYP structure, whereas PM3(Relax) refers to values derived from an optimized structure.

Table 8. Regression Parameters Derived from the Plot in Figure 3

	slope	R^2
notrans	0.9985	0.9979
trans	0.9978	0.9980
PM3(Fix)[a]	0.8737	0.9871
PM3(Relax)[b]	0.9207	0.9933

[a] The PM3(Fix) values have been derived using the B3LYP structure. [b] PM3(Relax) refers to values derived from a structure optimized with PM3(tm).

Discussion

Molecular mechanics parametrization has long been a tedious process, both for conventional organic molecules and the more complex inorganic and organometallic systems.[33] Attempts to automate the process has frequently been limited to certain types of data, or to one specific force field. Norrby and Liljefors[22] have recently published a method of adding parameters to an existing force field, using any available input data. This method allows an efficient parametrization and also an analysis of the parameter convergence.

The choice of input data is of great importance performing a parametrization. As the scope of the present force field is to allow not only precise predictions of coordination geometries, but also energies, it is not sufficient to use X-ray data alone. To improve the accuracy in the determination of force constants, we have included quantum chemical data in the form of a Hessian.[34] Quantum chemical calculations can be performed with high accuracy in both geometries and in energy second derivatives and should therefore routinely be used in MM parametrizations. One advantage of including QC Hessians is the large amount of input data that can be obtained. Another advantage is that additional terms such as out-of-plane bending parameters and stretch−bend interactions could be included and parametrized with high accuracy. The use of QC data will increase the transferability of the derived force field to new distorted structures.

X-ray structures are readily available from the Cambridge Crystal Data Base (CCDB) and were utilized under the assumption that crystal packing effects are minor and nonsystematic. In general, distorted structures favor an accurate determination of force constants. In our parametrization a wide range of different Ru−polypyridyl complexes have been included, several having large distortions from an ideal octahedral structure due to strained ligands or steric interactions between ligands. The energy excess calculated in Table 7 shows a good qualitative correlation with the *R* values of the X-ray data ($R^2 = 0.44$, excluding ZADLAR, which is binuclear). This behavior could be expected from a well-parametrized force field. The energy excess of complex ZADLAR is consistently very high. This is the only binuclear complex in the study. In the crystal structure, the two metallic centers are fairly close together and stabilized by counterions. The molecular mechanics calculations have been performed in vacuo and without any counterion, resulting in a severe repulsion between the two cationic centers. For most other complexes, especially those with low *R* values, the energy excess lies around 20 kJ/mol when a harmonic tethering has been applied.

Monoterpyridine complexes pose an important parametrization problem. The center nitrogen in these complexes is, in the X-ray structures, found to be closer to ruthenium than ordinary nitrogens of less rigid ligands. As a result of this bond shortening, the ligand trans to this bond is bound at a distance longer than usual. This effect is commonly called the trans influence and has electronic causes. The trans influence of a moderate π-acceptor ligand like bpy serves to remove electron density from the metal π-system on the opposite side of the metal ion and, if the ligand trans to the central terpyridine ring *also* is a π acceptor, a shifted electron distribution within a d-type orbital might be envisioned.[35] This phenomenon is particularly pronounced in the monoterpyridine complexes used in the parametrization and is of course absent where all the nitrogens are of the same type. To solve this problem, a parameter had to be added to the force field to improve the predictions of $N_{sp^2}\cdots N_{sp^2}$ trans distances. Since stretch−stretch terms are not available in the MM3* paradigm, one reasonable option was to include an additional direct $N_{sp^2}\cdots N_{sp^2}$ trans force constant and an ideal bond length for this distance. This resulted in a large decrease in the Ru−N_{sp^2} force constant from 2.68 to 1.47 to compensate for the additional parameters that are linearly dependent. The force constant of the new trans parameter was 0.64 and the ideal bond length was 4.12 Å whereas the ideal Ru−N_{sp^2} remained at 2.08 Å. As the ideal trans bond length is less than twice that of a single bond, all complexes are inherently strained. Only when the Ru−N bond is shortened to less than 2.04 Å will the trans influence become repulsive (i.e., the effective ideal bond length of the trans bond will become longer than 2.08 Å).

It can be seen in Tables 2−5 that most parameters are well determined, that is, the values are large compared to the corresponding ranges. A few exceptions should be noted. The

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(34) For earlier uses of Hessians in force field parametrization, see for example: (a) Dasgupta, S.; Goddard, W. A., III. *J. Chem. Phys.* **1989**, *90*, 7207. (b) Maple, J. R.; Hwang, M.-J.; Stockfisch, T. P.; Dinur, U.; Waldman, M.; Ewig, C. S.; Hagler, A. T. *J. Comput. Chem.* **1994**, *15*, 162. (c) Hwang, M.-J.; Stockfisch, T. P.; Hagler, A. T. *J. Am. Chem. Soc.* **1994**, *116*, 2515. (d) Dasgupta, S.; Yamasaki, T.; Goddard, W. A., III. *J. Chem. Phys.* **1996**, *104*, 2898.

(35) For a discussion of the trans effect, see for example: (a) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon: Oxford, 1984; p 1352. The problem of unequal bond lengths to electronically similar ligands has been addressed previously in inorganic molecular mechanics, in particular in relation to the Jahn−Teller effect. For examples, see: (b) Manchanda, R.; Zimmer, M.; Brudvig, G. W.; Crabtree, R. H. *J. Mol. Struct.* **1994**, *323*, 257. (c) Comba, P.; Zimmer, M. *Inorg. Chem.* **1994**, *33*, 5368. (d) Burton, V. J.; Deeth, R. J.; Kemp, C. M.; Gilbert, P. J. *J. Am. Chem. Soc.* **1995**, *117*, 8407.

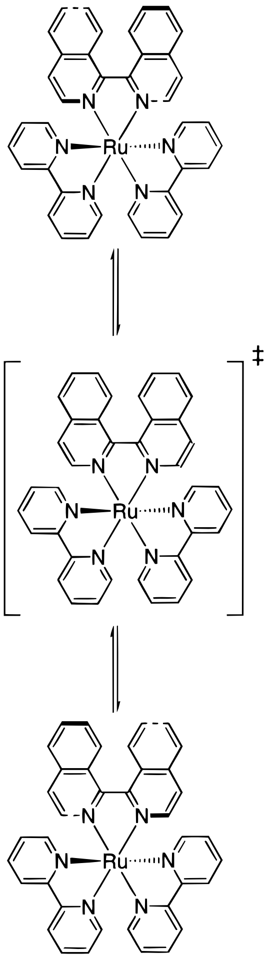

Figure 4. Isomerization of Δ/Λ-(δ/λ-1,1′-biisoquinoline)bis(2,2′-bipyridine)ruthenium(II) via a planar η^2-1,1′-biisoquinoline ligand.

reference value for the Ru−N−H angle is large and uncertain, due to a lack of proper structural data (vide supra). However, this parameter has no influence on the main target molecules. Of more concern is the low quality of the torsion parameter between Ru and ortho-alkyl substituents ($\mathrm{Ru{-}N_{sp^2}{-}C_{sp^2}{-}C_{sp^3}}$). This parameter influences, for example, the structures of neocuproin complexes (e.g., KEFCON, Figure 1).

In this work, we have succeeded to accurately predict coordination geometries of $\mathrm{Ru^{II}}$−polypyridyl complexes. The molecular mechanics model used has an rms error of only 0.02 Å in the $\mathrm{Ru{-}N_{sp^2}}$ bond for the entire ensemble of complexes used in the parametrization. This should be compared to the standard deviation in the reported X-ray structures of $[\mathrm{Ru(bpy)_3}]^{2+}$ that is 0.0094 Å for the $\mathrm{Ru{-}N_{sp^2}}$ bond.

As an illustrative example of the strength and accuracy of the present approach, we have applied our force field to the diastereomeric equilibrium for $[\mathrm{Ru}(2,2'\text{-bipyridine})_2(1,1'\text{-biisoquinoline})]^{2+}$. In this complex, the 1,1′-biisoquinoline is twisted due to steric interactions between the two isoquinoline units. This results in an axis of chirality. Together with the bis(2,2′-bipyridine) part of the complex, also possessing chirality, this results in the formation of diastereomers (Figure 4). The isomerization has been studied thoroughly by Ashby et al.[36] They have determined the equilibrium constant (2.71 at 50 °C, $\Delta G_{50}{}^\circ = 2.7$ kJ/mol) together with the activation barriers for the diastereomeric inversion of Δ/Λ-(δ/λ-1,1′-biisoquinoline)bis(2,2′-bipyridine)ruthenium(II) ($\Delta G_{50}{}^{\ddagger} = 79$ kJ/mol for the conversion from the major diastereomer).

Using the current force field we were able to calculate the energy difference between the two diastereomers to 3.0 kJ/mol (ignoring possible entropy contributions), very close to the experimental value of 2.7 kJ/mol. This indicates that the force field is indeed very accurate.

The mechanism for this diastereomeric isomerization have been suggested to involve a planar η^2-1,1′-biisoquinoline ligand.[36] Although the rotational barrier for an isomerization of the free ligand proceeding via syn geometry is expected to be very high, coordination of the ligand to ruthenium should lower this barrier due to a more favorable coordination geometry for the ruthenium bound nitrogens of the 1,1′-biisoquinoline ligand.

To analyze the probability for this mechanism we estimated the activation barrier for this reaction. The transition state was determined by a dihedral drive calculation of the 1,1′-biisoquinolin ligand (Figure 4).[37] The barrier for this mechanism was estimated to be ca. 100 kJ/mol, 30 kJ/mol above the experimentally determined barrier of 70 kJ/mol ($\Delta H^{\ddagger}$). This indicates that a mechanism involving a syn transition state indeed could be possible. In addition, the barrier for enantiomeric interconversion of the free 1,1′-biisoquinoline ligand was calculated. This barrier was found to be ca. 150 kJ/mol for the syn transition state. It appears to us that, ruthenium coordination of the 1,1′-biisoquinoline ligand significantly lowers the syn transition state energy. Although the activation barrier predicted by the molecular mechanics calculations is rather high compared to the experimentally determined value, the calculations support the conclusions by Ashby; coordination of 1,1′-biisoquinoline to ruthenium will result in a large decrease in the isomerization barrier.

One of the strengths of computational chemistry is the possibility to prognosticate and to facilitate rational molecular design. Supermolecular arrays composed of several units of varying functionality, together with a photosensitizer, are often flexible. The flexibility implies that great care has to be taken in their construction. Molecular mechanics offers a unique possibility to perform these initial precautions by means of fast geometry determinations of molecular candidates. The minimizations could easily be extended to include conformational searches and energy determinations including solvation effects. This permits calculations of NMR coupling constants and predictions of NOE's which are very useful for the characterization and structure determination of new complex molecules.

An alternative method, which was recently developed for determination of coordination geometries and energies, is based on semiempirical calculations and the PM3(tm) parametrization.[16] This method is, according to our experience, somewhat less accurate than the MM3* force field derived in this work. The main error in the semiempirical method is that force constants are systematically overestimated. This is obvious from a plot of the values in the semiempirical Hessian matrix vs the values derived from the B3LYP calculation (Figure 3) where the slope seriously deviates from unity (0.92). The slope is equal to the square root of the scaling factor that should be

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[36] (a) Ashby, M. T.; Govindan, G. N.; Grafton, A. K. *Inorg. Chem.* **1993**, *32*, 3803. (b) Ashby, M. T.; Govindan, G. N.; Grafton, A. K. *J. Am. Chem. Soc.* **1994**, *116*, 4801. (c) Ashby, M. T. *J. Am. Chem. Soc.* **1995**, *117*, 2000.

[37] The ligand is not planar in the TS, but skewed. The transition state energy was estimated by driving the dihedral H···C−C···H from −30 to +30° (H, hydrogens that interfere in the TS; C, carbons interconecting the quinolines). This approach might give barriers that are too high.

Table 9. Correlation between the Lifetime of the ^{3}MLCT State and the Steric Strain of the Photosensitizer

entry no.	complex	ligand exchange energy[a] (kJ/mol)	lifetime of the ^{3}MLCT state (μs)	solvent[b]	T (K)	ref
1	Ru(bpy)$_3$	0	5.3	alc.	77	38d
2	Ru(6-methylbpy)$_3$	−73	4.1	alc.	77	38d
3	Ru(6,6′-dimethylbpy)$_3$	−156	2.5	alc.	77	38d
4	Ru(bpy)$_3$	0	0.92	AN	RT	39
5	Ru(3,3′-dimethylbpy)$_3$	−89	0.21	AN	RT	40
6	Ru(bpy)$_3$	0	1.15	alc.	RT	40
7	Ru(4,4′-dimethylbpy)$_3$	13	0.95	alc.	RT	40
8	Ru(5,5′-dimethylbpy)$_3$	15	0.35	alc.	RT	40
9	Ru(bpy)$_2$(py)$_2$ (cis/trans)[c]	−51/−102	0.0027	alc.	RT	41

[a] This is the energy for the isodesmic reaction: $\mathrm{RuL}_x^{2+} + 3$(2,2′-bipyridine) → Ru(2,2′-bipyridine)$_3^{2+}$ + xL. [b] Alc. refers to a 4:1 mixture of ethanol and methanol; AN, acetonitrile. [c] The configuration is not specified by the authors.

used to compensate for systematic errors in frequencies. In this case, a scaling factor of 0.85 should be used. In the case of ordinary HF calculations on organic compounds, the scaling factor is usually set to 0.89.[29] A comparison of the relaxation energies of the PM3(tm) method to the MM3* energies also indicates that the semiempirical method gives structures that are too stiff (Table 7). The semiempirical methods are slow compared to molecular mechanics and conformational searches for supermolecular complexes could be extremely time consuming.

The most important question concerning the photophysics of Ru^{II}−polypyridyl complexes is the puzzling correlation between coordination geometry and emission properties. The MM3* force field will hopefully emerge as an important tool in increasing the understanding of this relationship. Hitherto, the lack of quantitative information about the geometries of photosensitizers has been a problem. Molecular mechanics calculations can solve this problem and the calculated geometries and energies could serve as an important source of information. As an initial, simplistic approach to quantify the steric crowding in the complexes, we have utilized the MM to calculate the amount of steric/Coulombic energy that is required to bind the ligands to the metal. Included in this is the internal energy of the ligands as well as the energy of interaction between the ligands when coordinated. To perform isodesmic comparisons we have chosen the dissociation of [Ru(bpy)$_3$]$^{2+}$ as a reference reaction. This will yield the overall reaction: [RuL$_x$]$^{2+}$ + 3(2,2′-bipyridine) → [Ru(2,2′-bipyridine)$_3$]$^{2+}$ + xL.

The results in Table 9 show a promising correlation between the relative stability of a series of photosensitizers and the lifetime of the ^{3}MLCT emitting states. The most stable complexes in Table 9 have the most long-lived excited states. Complexes containing ligands substituted in positions such as the 6-position of 2,2′-bipyridine are less stable than the analogous complex with nonsubstituted ligands. This could for example be seen in the tris 6,6′-dimethyl-2,2′-bipyridine analogue (Table 9, entry 3) of the [Ru(bpy)$_3$]$^{2+}$ complex. Complexes of this type have been studied extensively and usually show short excited-state lifetimes.[14,38] Distortions of the coordination geometry due to steric strain within a ligand also tend to decrease the lifetime of the luminescent exited state. This effect is seen in [Ru(bpy)$_2$(3,3′-dimethyl-2,2′-bipyridine)]$^{2+}$ (Table 9, entry 5). All complexes containing monodentate ligands are known to have short excited-state lifetimes. This correlates with the calculated relative stability of Ru(bpy)$_2$(py)$_2$ that is found to be less stable than complexes having good emitting properties. Ru(5,5′-dimethylbpy)$_3$ shows a very interesting deviation from the overall trend in Table 9. Although the steric strain is very low in this complex, the excited state lifetime is still reduced. Further investigations of Ru^{II}−polypyridyl complexes by use of this new tool will probably yield a more complete picture of how the coordination geometry could effect photophysical and photochemical properties of this type of photosensitizers and photoelectron donors.

Conclusions

The molecular mechanics calculations presented in this paper appears to be a tool of significant utility. A qualitative correlation have been found between coordination geometry and emission properties for the ruthenium polypyridyl complexes examined in this paper. The accuracy in geometry determinations has been found to be very good. The application of the molecular mechanics force field to the diastereomeric equilibrium in [Ru(bip)$_2$(1,1′-biisoquinoline)]$^{2+}$ shows an excellent correlation to the experimental value of the equilibrium constant and thus the force field is well adapted to deal with both equilibria and kinetics. Since calculations are several orders of magnitude faster and cheaper than X-ray methods, and easily may be applied even *before* the synthesis is undertaken, it is very likely that the molecular mechanics will become a very useful tool for the further development of the field of ruthenium polypyridyl chemistry. The possibility of including solvation models in the calculations enables predictions of geometries in solution. This force field may also be of importance in the development of technologies based on this type of ruthenium polypyridyl photosensitizers.

Acknowledgment. Financial support from the Ernst Johnson Foundation, the Danish Medical Research Council, and Knut and Alice Wallenberg Foundation is gratefully acknowledged.

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