A MOLECULAR-ORBITAL-BASED MOLECULAR MECHANICS
APPROACH TO STUDY CONJUGATED SYSTEMS

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The Allinger's MM2 program has been extended to calculate conjugated systems
including N, O, and S hetero atoms.

The molecular mechanics (MM) or force field method has been shown to be a very reliable, fast, and efficient way of determining molecular structures, energies, and other properties for a wide variety of compounds.[1-3] There are several force fields for which extensive usage have been reported and are currently in use worldwide. However, it appears that the Allinger's MM2 force field is the most popular one at this time.[1-4] Efforts to extend MM2 to calculate conjugated systems by including a π-system molecular orbital (MO) treatment in calculations have been reported in several versions.[4] However, all of these reported MM2 extensions are limited to conjugated hydrocarbons. Theoretically, it is a rather straight-forward application to extend the same existing formalism to hetero conjugated systems by developing necessary MO and MM parameters. However, this appears to counteract the advance of science since it is well-known that the π-theory has severe limitations and the all-electrons (or, at least, all-valence-electrons) MO methods have been developed and employed extensively in the past decades. Furthermore, it has also become evident that there are systems which the current MM methods cannot simulate well by simply adding new parameters.[2,3] These unsatisfactory force field results may be due to special orbital inter-actions, which may not be described well by a simple π-electron theory.

A combination of MM and sophisticated MO methods seems to be a solution to those problems. In our proposed approach, MO calculations are performed to derive or to modify MM parameters in cases where there are doubts about the capabilities of usual MM methods, while MM calculations are used in the structural optimizations. This approach makes it more feasible to calculate large molecules since one can specify which portion of a molecule needs MO treatment. The CPU time required for MO calculations are drastically reduced by this approach which performs single point MO calculations and partial MO treatment.

As far as CPU time is concerned, it also appears to be logical to use a semiempirical molecular orbital method instead of the ab initio methods. The MNDO method has been arbi-trarily selected to test our methodology simply because of its popularity. In this work, we report calculated results for conjugated systems containing C, H, N, O, and S atoms.

In our current approach, the basic equations used are very similar to those used in MMPI[5] and MMPI76.[6] Namely, the natural bond length between atoms i and j, l_0, required by the force field is obtained from the linear relationship,

$$l_0 = l_I + l_{II} \bullet X \qquad (1)$$

where l_I and l_{II} are coefficients specific to atom types of i and j, X is the product of the calculated MNDO bond order and core Hamilitonian between the atom pair i and j. This linear relationship is justified in light of model studies of several appropriate ground-state molecules.[7] The stretching force constants, k_s, between atoms i and j are calculated by

$$k_s = k_I + k_{II} \bullet X \qquad (2)$$

where k_I and k_{II} are empirical coefficients specific to atom types i and j. The two-fold torsional constant, V_2, across a double bond is employed to measure the π-bond disruption as rotation occurs about the bond. The two-fold torsional constants are written as follows

$$V_2 = V_I \bullet f \qquad (3)$$

where V_2 and f are empirical constants. The value of V_I is specific to the atomic types of those four atoms which define a dihedral angle, while f is expressed as an arbitrary function of X. The exact f function used is not concerned in this paper, since we limit our discussions to planar systems.

A computer program (MOMM) has been developed to test this approach; the modified MM2 program can create a subprocess to do MNDO calculations, which returns the derived X matrix. The optimization procedure is basically as follows. All force field parameters are initially assigned from the input data. Force field parameters developed earlier[6-8] are carried over here. A MNDO calculation is then performed for the portion of molecules which is designated for MO treatment and related force field parameters are modified accordingly. The steric energy is then minimized with respect to geometry. If the geometry has been significantly changed during the minimization step, the MNDO calculations are repeated and all the parameters dependent on the MO calculations are reassigned. The MM-MNDO cycle is repeated until total self-consistency is achieved. It usually takes less than five such cycles to reach self-consistency.
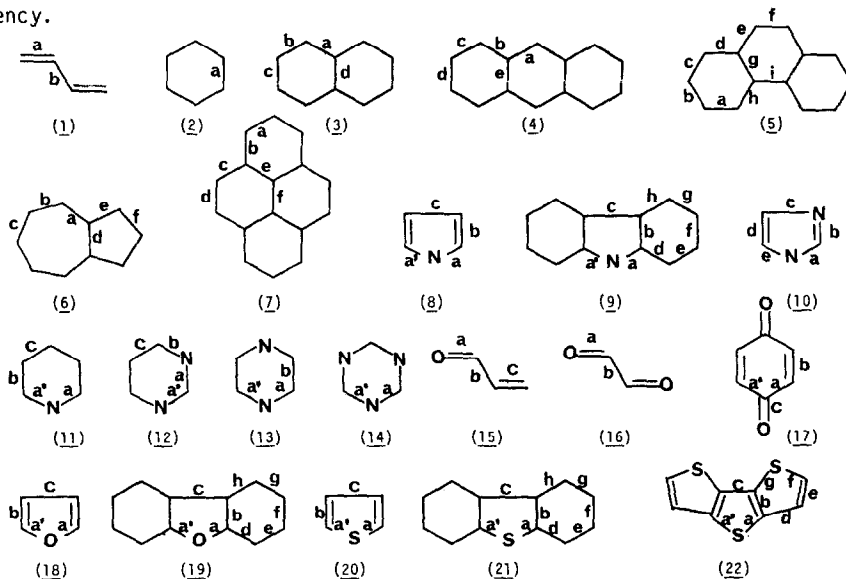

Diagram 1

TABLE I. EXPERIMENTAL AND THEORETICAL STRUCTURES

Struc. Param.	Experi- mental	This Work	Struc. Param.	Experi- mental	This Work	Struc. Param.	Experi- mental	This Work	Struc. Param.	Experi- mental	This Work
trans-Butadiene (1)[a]			Pyrrole (8)[a]			Pyrimidine (Cont'd)			Dibenzofuran (Cont'd)		
a	1.344	1.340	a	1.370	1.347	ab	115.5	116.1	g	1.389	1.407
b	1.467	1.469	b	1.382	1.391	bc	122.3	121.7	h	1.384	1.376
ab	122.9	122.0	c	1.417	1.435				aa'	104.1	106.2
			aa'	107.7	110.6	Pyrazine (13)[m]			ab	112.3	112.0
Benzene (2)[b]			ab	109.8	108.4	a	1.339	1.334	bd	123.0	119.3
a	1.399	1.400				b	1.403	1.419	de	116.7	118.7
			Dibenzopyrrole (9)[i]			aa'	115.6	116.7	ef	120.9	121.1
Naphthalene (3)[c]			a	1.393	1.364	ab	122.2	121.6	fg	121.9	120.7
a	1.422	1.432	b	1.408	1.430				gh	117.9	117.4
b	1.371	1.374	c	1.477	1.450	s-Triazine (14)[n]					
c	1.412	1.426	d	1.403	1.393	a	1.338	1.356	Thiophene (20)[s]		
d	1.420	1.415	e	1.373	1.397	aa'	113.2	113.8	a	1.714	1.726
			f	1.393	1.414				b	1.370	1.346
Anthracene (4)[d]			g	1.392	1.400	Acrolein (15)[o]			c	1.424	1.457
a	1.405	1.406	h	1.391	1.384	a	1.208	1.221	aa'	92.2	90.3
b	1.444	1.444	aa'	108.3	110.3	b	1.478	1.474	ab	111.5	113.2
c	1.375	1.363	ab	109.7	108.8	c	1.335	1.340			
d	1.418	1.437	bd	121.9	119.4	ab	124.0	125.0	Dibenzothiophene (21)[t]		
e	1.433	1.427	de	115.6	118.7	bc	121.0	121.1	a	1.740	1.732
			ef	123.9	121.2				b	1.409	1.414
Phenanthrene (5)[e]			fg	120.1	120.8	Glyoxal (16)[o]			c	1.441	1.457
a	1.401	1.385	gh	117.9	117.6	a	1.207	1.222	d	1.384	1.386
b	1.394	1.412				b	1.525	1.516	e	1.384	1.405
c	1.386	1.381	Imidazole (10)[j]			ab	121.2	119.4	f	1.385	1.405
d	1.423	1.423	a	1.343	1.338				g	1.370	1.404
e	1.453	1.446	b	1.326	1.286	p-Benzoquinone (17)[p]			h	1.392	1.391
f	1.350	1.353	c	1.378	1.424	a	1.477	1.474	aa'	91.5	91.2
g	1.420	1.421	d	1.358	1.389	b	1.322	1.338	ab	112.3	113.2
h	1.409	1.425	e	1.369	1.361	c	1.222	1.223	bd	121.6	121.0
i	1.465	1.464	ab	111.2	117.4	aa'	117.1	116.7	de	117.8	118.6
			bc	105.3	101.1	ab	121.1	121.6	ef	121.6	120.6
Azulene (6)[f]			cd	109.8	110.2				fg	120.5	120.6
a	1.383	1.385	ae	107.2	105.8	Furan (18)[q]			gh	120.0	118.7
b	1.406	1.394				a	1.362	1.362			
c	1.403	1.396	Pyridine (11)[k]			b	1.361	1.371	Dithieno[3,2-b:2', 3'-d]thiophene (22)[u]		
d	1.501	1.465	a	1.340	1.334	c	1.431	1.464	a	1.730	1.722
e	1.418	1.425	b	1.396	1.408	aa'	106.6	105.6	b	1.380	1.380
f	1.399	1.408	c	1.394	1.401	ab	110.7	112.3	c	1.423	1.413
			aa'	117.0	118.2				d	1.414	1.434
Pyrene (7)[g]			ab	123.8	123.3	Dibenzofuran (19)[r]			e	1.344	1.360
a	1.395	1.398	bc	118.5	118.4	a	1.404	1.373	f	1.722	1.740
b	1.406	1.407				b	1.393	1.428	g	1.711	1.706
c	1.438	1.451	Pyrimidine (12)[l]			c	1.481	1.463	aa'	90.3	88.8
d	1.367	1.356	a	1.340	1.350	d	1.385	1.386	ab	113.0	114.4
e	1.425	1.417	b	1.340	1.333	e	1.388	1.404	bd	113.5	112.4
f	1.430	1.437	c	1.393	1.411	f	1.385	1.408	de	111.9	109.8
			aa'	127.6	127.3				ef	113.9	114.8
									fg	90.7	89.4

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To test the practical applicability of our approach and to derive necessary force field parameters, we first studied planar conjugated hydrocarbons (Diagram 1) by recomputing most of the structures which appeared in our earlier paper.[6] By adjusting the parameters, reasonable results compatible to the earlier work can be obtained. Comparison of experimental and theoretical structures are depicted in Table I. Rotational barriers for conjugated polyenes were also computed by using different f functions of eq. 3. The obtained results were also compatible to the earlier work but a generalized final format of f has yet to be determined.[7]

After satisfying the force field parameters for conjugated hydrocarbons, extensions to hetero conjugated systems were performed. Due to the limited amount of experimental data, several ab initio calculations were carried out on model compounds, essentially to provide necessary information for the force field development.[7] Comparison of these structural parameters between calculated values and experimental data are also presented in Table I. There is generally good agreement between calculated results and experimental data.

In summary, we have developed the MOMM program in an attempt to overcome the current MM2 limitations. The MNDO calculations are used to modify MM parameters and the geometry is then optimized under the derived force field. An iterative procedure is employed for this approach. Results for conjugated systems containing C, H, N, O and S atoms are satisfactory. Expansions of this approach to other systems are straightforward. Applications of MOMM to large (macro) molecules containing conjugated fragments are underway.

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