

INTERMOLECULAR POTENTIALS OF EDA COMPLEXES BY SEMI-EMPIRICAL THEORY DISPERSION ENERGY TERMS IN THE PM3 METHOD

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Abstract: The recently developed PM3 parametrization scheme for MNDO-type calculations by Stewart is shown to give ground state properties (geometries, energies of formation) of the complexes formed between TCNE and a variety of aromatic donors in qualitative agreement with *ab initio* and available experimental results, provided appropriate dispersion energy terms are included. The method appears to yield geometries for EDA complexes suitable for electronic structure calculations.

INTRODUCTION

Despite the development of ever-more faster computers and the advent of ready-to-use *ab initio* programs the calculation of molecular complexes even of moderate size will remain, for years to come, a domain of empirical or semi-empirical methods. These methods, as a consequence of suitable parametrization, are able to avoid some of the pitfalls of the *ab initio* method, as there are the basis set superposition error,¹ the tendency to underestimate exchange repulsion caused by basis functions decaying too rapidly,² and the error due to neglect of correlation energy. Correlation energy, or rather the lack of it, is thought to be the reason that no stable complexes are calculated for the face-to-face interaction between two ethylene³ or benzene molecules⁴ at the single-determinant Hartree-Fock level; even with the very flexible 6-31G* basis no potential energy minimum develops between two approaching ethylenes.⁵ Electron donor acceptor (EDA) complexes, e.g. between benzene and carbonyl cyanide, do not fare much better:⁶ calculated binding energies are much too small and distances too large, a consequence of inadequate representation of the intermolecular attraction.

In Hartree-Fock theory to account for correlation energy in the supermolecule approach of molecular complexes one can either perform a conventional CI calculation or use a Moller-Plesset type perturbation approach⁷ both of which are rather time-consuming. There are other ways to improve on *ab initio*, viz. the use of empirical energy terms to substitute or supplement the quantum-mechanical calculation.⁸ In the Buckingham-Fowler model⁹ the electrostatic interaction between two molecules is calculated by using sets of distributed multipoles obtained from *ab initio* wave functions of the monomers. Morokuma from his method of partitioning SCF interaction energies¹⁰ has derived dispersion energy terms from second-order perturbation theory¹¹ which are added onto a normal *ab initio* calculation of the supermolecule.¹² More in line with this latter approach is the work by Huiszoon and Mulder¹³, who fitted a long range

attractive $r \cdot \exp(-6)$ term to *ab initio* calculated dispersion interaction coefficients. Their parameters which were corrected later¹⁴ have been used since in *ab initio*⁴ as well as in semi-empirical calculations of intermolecular interactions¹⁵.

Much effort has gone into applying semi-empirical methods to the calculation of molecular complexes: CNDO/2¹⁶, CNDO/S¹⁷, PPP¹⁸, INDO¹⁹, as well as the more recent MNDO and AM1 models^{20,21} all have been used for this purpose. It is well known that of these methods CNDO and INDO cannot be employed to optimize supermolecule structures because of their neglect of diatomic differential overlap. This leads to a loss of exchange repulsion and as a consequence calculated intermolecular distances are much too small. That MNDO and AM1 on the other hand are able to sufficiently reproduce repulsion between molecules or molecular fragments is due to their extensive parametrization, especially with respect to electrostatic repulsion. Intermolecular potentials have been calculated by both *ab initio* and MNDO.⁵ Inclusion of dispersion via Mulder's parameters¹⁵ resulted in satisfactory potential energy curves for several EDA complexes; with AM1, the third-generation parametrization scheme,²² on the other hand, no geometry optimization was possible.

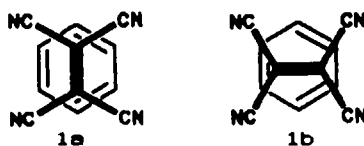
MNDO today appears to be one of the most widely used semi-empirical methods²⁰. Recently Stewart has published an improved parameter set for MNDO and AM1 called MNDO-PM3²¹, which significantly reduces the error in calculated heats of formation. Since this method can be expected to find widespread acceptance we felt it appropriate to investigate the performance of MNDO-PM3 augmented with atomic dispersion energy parameters. The complexes we have chosen for this study, different aromatic systems and tetracyanoethylene (TCNE), reflect our experimental approach to EDA complex electronic structure: chiral derivatives of anthracene make the complexation with TCNE amenable to chiroptical techniques. By studying such complexes by UV and CD spectroscopy we hope to reveal more information about the interaction between the components.

METHOD

For the monomers either X-ray (TCNE) or MMP2-optimized structures (donor molecules) were used; these structures remained unchanged during optimization of the different complexes. For calculating the intermolecular potentials we employed PM3 as well as other methods (MNDO²², AM1²³, both from QCPE²⁴ and *ab initio* as Gaussian 86²⁵). Atomic dispersion parameters were those published by Hobza and Zahradnik.²⁶ All conformations were strictly cofacial, i.e. the planes of the two π -components were always kept parallel. Energy calculations were performed with varying distances between the molecular planes, until a minimum could be located. In addition, some in-plane motions were also considered.

RESULTS AND DISCUSSION

Because of its small size the benzene-TCNE complex lent itself not only to the different semi-empirical and standard STO-3G calculations, but to split valence-orbital basis sets as well (STO-3-21G and STO-4-31G). These are the most advanced calculations reported so far for this complex. Watanabe²⁷ calculated this complex with the same basis, but the intermolecular



distance was not optimized, and the number of two-electron-integrals was considerably reduced.

There are two conformations with over-all C_{2v} -symmetry that are interconverted by a 30° rotation of either component about the principal axis (1a, 1b). Energies and equilibrium distances obtained by the different methods are compared in Table 1. Binding energies range from 0.27 kcal/mol (MNDO) to 11.38 (STO-3G with dispersion energy added); only the *ab initio* split-valence basis sets give energies that seem realistic even without added dispersion

Tab. 1: Energies of formation, E, and equilibrium distances, R, of benzene-TCNE complexes

method ^a	reference energy ^b	geometry 1a		geometry 1b	
		E ^c	R ^d	E ^c	R ^d
MNDO	171.2641	-0.27	500	-0.28	510
MNDO/D		-3.12	380	-3.12	380
AM1	175.4579	-0.71	450	-0.71	450
AM1/D		-	-	-	-
PM3	193.9242	-0.70	450	-0.70	450
PM3/D		-7.10	310	-7.12	310
STO-3G	-667.159050	-1.03	380	-1.02	380
STO-3G/D		-11.38	300	-11.31	300
STO-3-21G	-671.837584	-4.34	350	-4.15	360
STO-4-31G	-674.610192	-4.14	360	-4.10	360

^a/D signifies added dispersion; ^bcalculated sum of SCF-energies of components (no interaction), in kcal/mol for the semi-empirical, in a.u.'s for the *ab initio* methods; ^cin kcal/mol; ^din pm.

energy when compared with the experimental heat of formation which is 6.6 ± 0.3 kcal/mol in the gas phase or rather the binding energy which is 0.6 kcal/mol less.²⁰

In Fig. 1 the potential energy curves obtained by the three *ab initio* basis sets for the complex 1a are shown for comparison; also, the PM3 curve is included. Split-valence bases generally give SCF energies larger than STO-3G,²⁰ because of the presumed tendency of these bases to overestimate charge effects (total charge on TCNE at 320 pm distance is $.004$, $.018$, and $.016 e$ for STO-3G, 4-31G, and 3-21G, respectively). Obviously, electron density can transfer into the opposite fragment without experiencing sufficient repulsion, a consequence of both the greater range and flexibility of the split basis. Another indication of the somewhat unrealistic charge distribution obtained with this basis is the fact that the energy of the LUMO (which is, of course, mostly TCNE-based) actually drops upon complexation; only in STO-3G and in PM3 the energy of this MO rises, as one would expect.

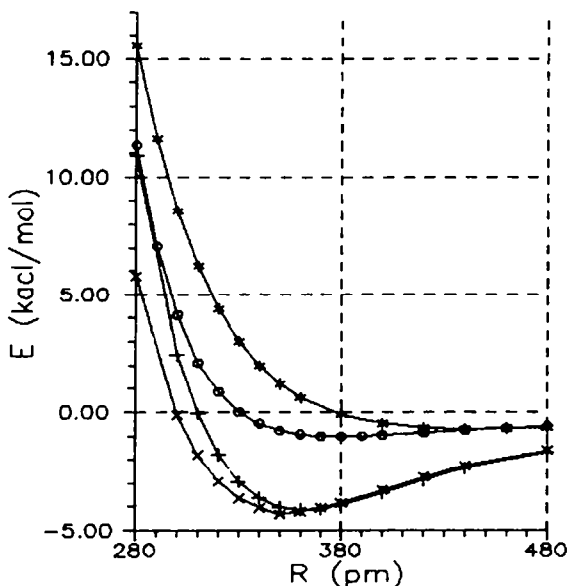


Fig. 1: SCF energies of benzene-TCNE complex (1a) as a function of intermolecular distance R. (Δ - Δ), PM3; (o-o), STO-3G; (x-x), STO-3-21G; (+-+), STO-4-31G.

STO-3G, on the other hand, underestimates repulsion at these distances due to the rapid decay of the wave-function,^{1,30} so the potential energy function turns out to be rather shallow. Compared to STO-3G PM3 is more repulsive except at very long distances; there is a crossing of the two potential curves at 380 pm.

Calculated energy differences between 1a and 1b are very small, as expected for what is essentially a 6-fold rotational barrier. All *ab initio* methods favor 1a slightly over 1b, while the opposite is true for the semi-empirical methods. AM1-calculated interaction energies are significantly larger than MNDO, a direct consequence of parametrization. AM1 differs from MNDO only in the enlarged core repulsion function, containing additional attractive and repulsive Gaussian functions. This is supposed to make up for known weaknesses of MNDO,

e.g. failure to reproduce hydrogen bonds. In contrast, electronic energy calculations are identical, except, of course, for the parameters employed. This shows in our calculations: the difference in electronic energy between AM1 and MNDO stays almost constant over the whole intermolecular distance covered (800 to 260 pm); in contrast, the core-core repulsion calculated by AM1 drops rapidly compared to MNDO at distances below 350 pm, leading to increased binding energies in this region. PM3 which also utilizes the expanded core repulsion function gives results identical with AM1 at the calculated equilibrium distance; at shorter distances, however, the AM1 energies rise much slower than the one calculated by PM3. This is of major consequence when we consider the addition of dispersion energy terms (see below).

To study the influence of configuration interaction we performed extensive AM1-CI calculations. Using a window of 10 MO's (which is necessary to ensure the inclusion of all relevant n-orbitals of the two components, viz. 4 MO's for benzene, 2 MO's for TCNE,) and 1500 up to quadruply excited configurations, the stabilization of 1a relative to isolated benzene and TCNE amounts to only .24 kcal/mole, a result worse than without CI and undoubtedly due to an unbalanced description of electron correlation in the complex vs. the components. With a smaller number of excited configurations, no stabilization of the complex was obtained at all. This unsatisfactory performance of CI in calculations of this kind has been noted before¹⁰ and led to its substitution by dispersion energy terms in the first place.

The dispersion energy is obtained independent of the model used to calculate the electronic structure of the complex; it is a term that decreases monotonically with decreasing intermolecular separation. All energy minima are therefore shifted towards smaller distance, the degree

depending only on the steepness of the potential energy function. The results are displayed in Fig. 2; calculated values for the equilibrium geometries are given in Table 1. The small STO-3G basis set gives rather large interaction energies of more than 11 kcal/mol; also, the cal-

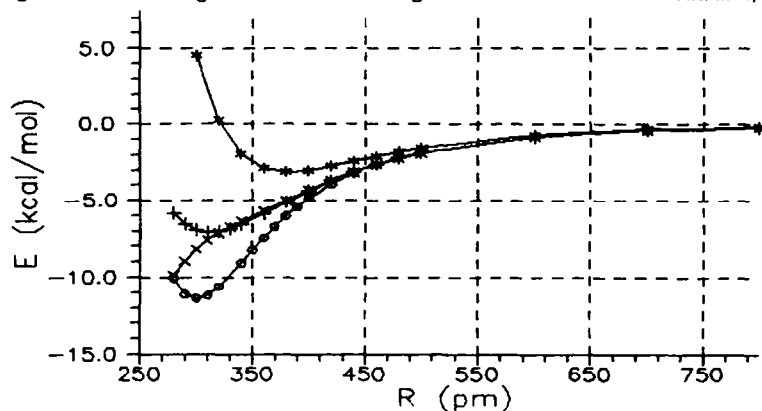
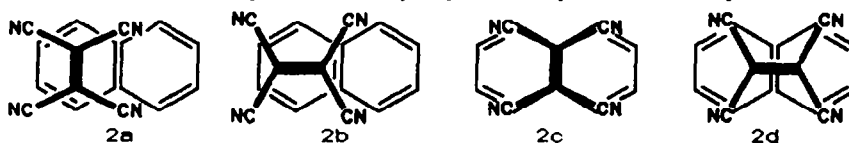


Fig. 2: Binding energy E of 1a as a function of intermolecular distance R . (*-*), MNDO; (+--+), PM3; (x-x), AM1; (o-o), STO-3G, all calculated with dispersion energy.

culated distance of 300 pm seems to be a rather small value. Due to the shallow potential energy curve calculated with AM1 no minimum is obtained when dispersion terms are added: the system collapses. MNDO gives a minimum, which is, however, rather flat (binding energy of about 3 kcal/mole at 380 pm). Between these two methods PM3 appears to present an acceptable compromise (7.1 kcal/mol at an equilibrium distance of 310 pm), its energy curve running almost parallel to the STO-3G curve.

For the naphthalene-TCNE complex an X-ray crystal analysis has been performed:³¹ one of



the conformations found is close to the ideal geometry 2a, with an intermolecular separation of 329 pm. The binding energy in the gas-phase has been determined (7.1 kcal/mol²⁷), somewhat larger than for the benzene complex. We have optimized the internuclear distance of the four structures 2a through 2d with STO-3G and PM3 including dispersion energy terms. In Tab. 2 binding energies and equilibrium distances are shown and, for a given intermolecular distance (320 pm) the different energy terms that make up the total energy. In this way a comparison of the methods applied is more meaningful.

Of the four conformations 2a is found to be the most stable by STO-3G and 2d by PM3; the difference in energy, however, between these and the least stable forms (2c and 2a) is very small, amounting to only 1.8 and 0.6 kcal/mol, respectively. PM3 favors both C_{2v} over the C_s geometries, just the opposite of what STO-3G does. The term responsible for this is the dispersion energy, which is larger for the more crowded geometries, just like the nuclear repul-

sion, which has a similar distance dependence. Subtracting this term from the binding energy gives the SCF energy, which, according to both methods, is more favorable for the less symmetric structures 2a and 2b.

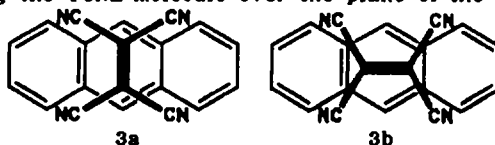
Tab. 2: Energy components of naphthalene-TCNE complexes at 320 pm intermolecular distance and binding energies at equilibrium distances

energy term ^a	2a		2b	
	STO-3G	PM3	STO-3G	PM3
nucl. rep. ^b	1358.692382	16058.5306	1358.691323	16057.3583
electronic ^b	-2176.621967	-18720.0701	-2176.620742	-18718.9091
SCF ^b	-817.929585	217.2595	-817.929419	216.9991
dispersion ^c	-14.434	-14.434	-14.485	-14.485
binding ^c	-12.924	-8.718	-12.870	-9.030
.....				
binding ^{c,d}	-13.921	-8.718	-13.524	-9.030
distance	300	320	300	320
energy term ^a	2c		2d	
	STO-3G	PM3	STO-3G	PM3
nucl. rep. ^b	1371.206785	16202.9856	1371.347580	16203.3282
electronic ^b	-2189.133261	-18864.4925	-2189.277094	-18864.8403
SCF ^b	-817.926475	218.0121	-817.927514	217.8900
dispersion ^c	-15.597	-15.597	-15.710	-15.710
binding ^{c,d}	-12.135	-9.120	-12.900	-9.364
.....				
binding ^d	-12.135	-9.120	-12.987	-9.364
distance	320	320	310	320

^acalculated at 320 pm distances between molecular planes; ^ba.u.'s for STO-3G, eV for PM3 (core repulsion); ^cat equilibrium distance (entry below, in pm).

The binding energy presents a delicate balance between (repulsive) nuclear and (attractive) electronic energy terms, of the two components compared with the complex. Considering that the semi-empirical and the *ab initio* method yield absolute values for these terms differing even in magnitude, it is surprising how close the relative energies agree: the order of decreasing nuclear repulsion and electronic energy (2d, 2c, 2a, 2b) is identical according to both methods. Despite this the two methods come to different results with respect to the SCF-energies because of the subtle differences involved.

Nothing is known concerning the binding energy or geometry of the anthracene-TCNE complex. By rotating and by moving the TCNE molecule over the plane of the aromatic system



we found 3a the most stable conformation by STO-3G and 3b by PM3.

In Fig. 3 the potential energy curves for the naphthalene and the anthracene complexes with TCNE on the basis of STO-3G and PM3 are compared. The correspondence between this semi-empirical and the *ab initio* method is again evident: both favor the anthracene over the

naphthalene complex (and the latter over the benzene complex), and calculated STO-3G binding energies are always larger, by about the same factor. No high-quality *ab initio* calculations were possible for systems this size.

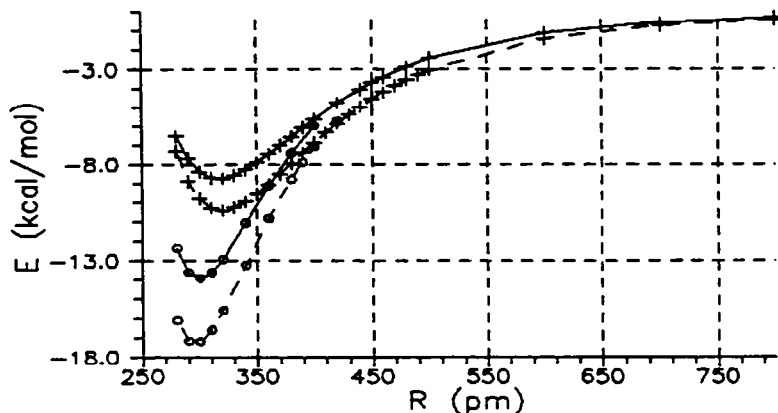
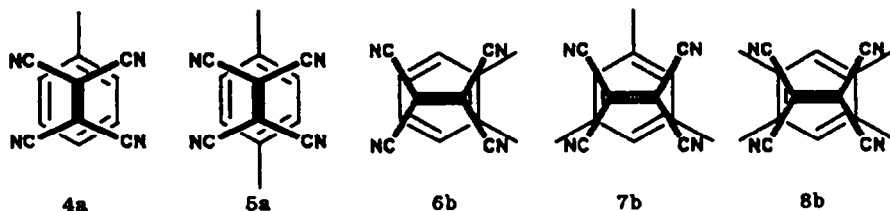


Fig. 3: Binding energy E of naphthalene-TCNE complex, 2a (—) and anthracene-TCNE complex, 3a (---) vs. intermolecular distance R . Circles correspond to STO-3G, crosses to PM3 calculations, all including dispersion energy.

As a final test for the validity of the proposed method we have calculated the binding energies of TCNE with several methyl-substituted benzenes, for which energies of formation have been determined.²² Again only the intermolecular distances were varied, keeping the two molecules in parallel planes. For each complex, two different geometries were calculated in which the TCNE molecule was rotated by 90° , except for 6 for which there were three starting geometries; only the most stable conformations are shown below.



Equilibrium distances and the energy terms making up the total binding energies are given in Table 3. All calculated distances lie between 310 and 330 pm, which seem to be reasonable values considering the experimental geometry of the naphthalene-TCNE complex. Also, calculated binding energies represent experimental trends very well.

Introduction of methyl groups lowers the SCF energy of the benzene molecule substantially. Nevertheless, SCF binding energies for identical distances (not shown in the Table) rise in going from 1 to 8, because the complexes get more crowded, and the increase in nuclear repulsion is not balanced by an equal increase in electronic energy. However, since the dispersion energy becomes more negative with the larger systems over-all binding energy increases from 1 to 8, in general agreement with experiment.

The wrong order of stabilities is calculated for the two isomeric xylene-TCNE complexes.

According to our calculations the ortho-isomer **6** has an intermolecular distance of 320 pm due to unfavorable interaction of the TCNE molecule with the two methyl groups (no geometry optimization was performed with respect to methyl torsion). In the para-isomer **5** the compo-

Tab. 3: Equilibrium distances^a and energy terms^b of TCNE complexes

	1b	4a	5a	6b	7b	8b
distance	310	310	310	320	330	330
SCF energy	200.130	191.650	183.180	183.383	172.396	166.101
SCF binding energy ^c	6.18	6.54	6.87	6.26	4.80	5.69
dispersion energy	-13.30	-14.72	-16.12	-14.66	-13.90	-15.43
binding energy	-7.12	-8.18	-9.25	-8.40	-9.10	-9.75
expt. energy. ^d	-6.0	-6.65	-7.42	-7.80	-9.09	-10.12

^ain pm; ^bin kcal/mol; ^cSCF energy minus sum of SCF energies of components; ^dref.32.

nents approach to within 310 pm which makes, of course, for a large gain in dispersion energy. Either moving the TCNE molecule in **6** away from the two methyl groups, or tilting its plane (motions not effective in lowering the energy of **6**) should considerably stabilize this complex. We have applied only two criteria, binding energies and intermolecular distances, to assess the validity of the method we propose. These criteria, as judged from the sparse experimental data available, are met for the TCNE complexes. We have looked only superficially at the electronic structures of the complexes and found the data controversial. The PM3-calculated total negative charge on the TCNE fragment at 320 pm distance from the aromatic increases from .002 to .0026 to .0038 e in going from benzene (**1a**) to naphthalene (**2a**) to anthracene (**3a**); LUMO destabilization for the complexes in the same order increases from .11 to .23 to .24 eV. Both these sequences indicate increasing interaction between the two components; however, HOMO energy shifts do not follow a clear pattern at all, possibly because other lower lying orbitals are involved in this stabilization as well.

We would like to make one final point regarding the distinction between a molecular complex and a molecule proper. From the standpoint of SCF-theory, i.e. within the variational approach to molecular structure calculation, there is no principle difference between these two; most important, the correlation energy is missing in both cases at the single determinant Hartree-Fock level. For the calculation of molecular complexes this is known to present a serious flaw (*vide supra*); bonding may simply not occur. This deficiency does not show up with such consequence in molecular structure calculations where bonding is provided *per se* and where "only" potential functions may be changed somewhat.

The question to what extent atomic dispersion terms might suffice to substitute for CI calculations, especially in large flexible molecules, has to our knowledge never systematically been pursued. We are presently engaged in addressing this problem.

CONCLUSION

There is an obvious need for a fast and reliable method to calculate ground state geometries of EDA complexes (or, for that matter, of any molecular complexes). EDA complexes have been postulated as precursors in cycloaddition reactions, like the Diels-Alder reaction,³³ or in certain elimination reactions.³⁴ To what extent the stereochemistry of such reactions is determined by the preference of the precursor complex for certain conformations may not be known until a complete conformational analysis, most probably on the basis of theoretical methods, has been performed.

Using a well established set of atomic dispersion energy parameters to supplement semi-empirical schemes we have looked closely at the three presently most popular methods, MNDO, AM1, and PM3, to see how they describe simple aromate-TCNE complexes and find the following:

(i) MNDO underestimates bonding and gives complexes with intermolecular distances too large. As a consequence steric effects may be underrepresented.

(ii) AM1 gives potential energy curves which are not repulsive enough to prevent collapse of the components once the dispersion terms are added.

(iii) PM3 results are evidently more realistic than the above giving reasonable intermolecular distances; experimental (gas-phase) binding energies are slightly over-estimated.

Whether these conclusions hold in general and for weakly bound molecular complexes as well will have to be seen; preliminary calculations³⁵ on the co-facial ethylene dimer and on the benzene-ethylene complex using PM3 and Hobza's parameters have yielded reasonable binding energies (1.13 and 3.0 kcal/mol) and equilibrium distances (310 and 290 pm, respectively).

Calculations were performed at the Hochschulrechenzentrum Dulsburg.

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