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D. S. Galvão, Z. G. Soos, S. Ramasesha, and S. Etemad

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A parametric method 3 (PM3) study of *trans*-stilbene

D. S. Galvão

Universidade Estadual de Campinas, Departamento de Física Aplicada, 13081 Campinas, SP, Brasil and Bell Communications Research, Red Bank, New Jersey 07701

Z. G. Soos

Department of Chemistry, Princeton University, Princeton, New Jersey 08544

S. Ramasesha

Department of Chemistry, Princeton University, Princeton, New Jersey 08544 and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

S. Etemad

Bell Communications Research, Red Bank, New Jersey 07701

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We report a comparative modified neglect of diatomic overlap (MNDO), Austin method one (AM1), and parametric method 3 (PM3) study of *trans*-stilbene (*tS*) in its ground, excited (singlet and triplet), and ionic (positive and negative polarons and bipolarons) states. We have also calculated the barrier for ring rotation about the backbone single bond. Our results show that PM3 geometries are superior to MNDO and AM1, at least for *tS*. PM3 predicts, in contrast with MNDO, AM1 and even *ab initio* 3-21G, a coplanar structure for *tS*, in accordance with recent experimental data. Singlet and triplet energies obtained from heats of formation are in surprisingly good agreement with experimental data.

I. INTRODUCTION

Great scientific and technological interest in understanding the optical and transport properties of conducting polymer is reflected by the enormous amount of theoretical and experimental work in the last years.¹ This is especially true for the poly-*p*-phenylene vinylene (PPV). PPV combines unusual properties such as good morphology, high conductivity and strong fluorescence.^{2,3} Recently, good optical devices based on PPV have been reported.⁴⁻⁷

Based on fluorescence data Rauscher *et al.*⁸ have challenged the spectroscopic description of PPV in terms of band theory. They showed the photoconductivity peak spectra is not a band to band transition, but exciton-exciton annihilation leading to carrier generation. Their results suggest a more molecular than solid-state approach to PPV and also suggest the presence of strongly correlated electron-hole pairs, both in absorption and emission spectra. Similar conclusions have been reached by Obrzut and Karasz in an earlier work.⁹ They observed that the evolution of the absorption band toward the red part of the spectrum as the conjugation length increases, is not as expected from band theory. Instead, their results suggest that the 402 nm absorption band is the result of overlapping transitions from localized energy levels, rather than extended conjugation. Furthermore, Simpson *et al.*^{10,11} have recently used nuclear magnetic resonance (NMR) experiments to study ring rotations in undoped and doped PPV samples. Out-of-plane ring motion has been observed, including a 180° flipping motion of the phenylene rings about the backbone single bonds.^{10,11} The presence of these defects, interrupting overlap of P_z orbitals, decreases the effective conjugation length, and consequently leads to a more molecular than solid-state behavior.

These experimental data are an indication that in order

to understand the details of the PPV electronic processes a comparative study of its oligomers is desirable; in particular, a detailed analysis of *trans*-stilbene (*tS*) (Fig. 1) in its ground, excited, and charged states could be useful in relating molecular and PPV data. *tS* has played a fundamental role in the studies of photoisomerization of substituted ethylenes. There is an enormous amount of experimental work on it using quite different techniques (x-ray,¹²⁻¹⁶ supersonic jet expansion,¹⁷⁻¹⁹ transient resonance Raman,^{20,21} etc.). In spite of this some fundamental aspects, such as the coplanarity of the phenyl rings, remain controversial.²²⁻²⁶ From a theoretical point of view, many techniques have been used²⁷⁻³⁵ to investigate the electronic structure of *tS*, from simple Hückel to *ab initio* calculations. However, a combined detailed analysis of ground, excited, and charged *tS* states has only been reported recently, from valence bond-Pariser-Parr-Pople (VB-PPP)³⁴⁻³⁶ calculations.

There is no detailed experimental study on the electronic structure of PPV as a function of its oligomer lengths. From a theoretical point of view the size of long PPV oligomers (6-7 rings) precludes the use of *ab initio* methods, but this size is not prohibitive for the sophisticated semiempirical methods like the modified neglect of diatomic overlap (MNDO)³⁷ or Austin method one (AM1).³⁸ In fact, some MNDO and AM1 PPV studies have been reported.³⁹⁻⁴¹ MNDO and AM1 are semiempirical methods well suited for geometrical optimizations. They provide a good balance between quality and computational effort. They have been extensively used recently¹ in calculations of oligomers and polymers (band structure calculations) with good success. AM1 has been developed in an attempt to correct some MNDO weaknesses. In AM1, as in MNDO, all three-center nuclear attraction integrals are retained, but the tendency of the MNDO to

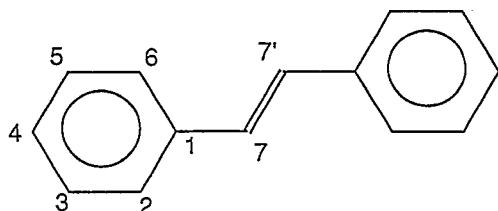


FIG. 1. *trans*-stilbene (*tS*) and the labeling used in this work.

overestimate the repulsion between atoms has been corrected by a suitable modification of the core repulsion function.³⁸ Recently, a new formulation of these methods has appeared, the parametric method 3 (PM3).⁴² PM3 has been developed in order to improve the MNDO and AM1 results. But, although it seems to be a consensus that AM1 is better than MNDO, there is an ongoing debate about the relative merits of AM1 and PM3.⁴²⁻⁴⁷

We report here a detailed MNDO, AM1, and PM3 study of the ground, excited (singlet and triplet), and ionic (± 1 and ± 2 , corresponding to positive and negative polarons and bipolarons, respectively) *tS* states. We have also calculated the barrier for phenyl ring rotation about the backbone single bond in the ground, excited, and ionic states. There are two motivations for our work. In addition to the intrinsic importance of *tS* and its relation to PPV, we wanted specific comparison, among PM3, AM1, and other theoretical techniques, including the first comparison for the excited states. The comparison of our results with the available experimental data and other theoretical calculations lead us to conclude that PM3 is better than AM1 in the present case.

In Sec. II we present the methodology; in Sec. III we present and discuss the results; Sec. IV contains a summary and conclusions.

II. METHODOLOGY

We have investigated the geometrical and energetic processes of *tS* using MNDO, AM1, and PM3 methods. We have performed a comparative study of its ground, excited, and charged states. We have also calculated the barrier for phenyl rotation about backbone single bond in ground, excited, and charged states. We have performed full geometrical optimization (including H atoms) calculations. For the rotational barrier calculations we have considered frozen and relaxed geometries. All results were obtained using a MOPAC-6.0 program,⁴⁸ UNIX version, DEC-3100 edition-1990.

III. RESULTS AND DISCUSSIONS

A. Ground state geometries

In Tables I and II we show bond lengths and bond angles data for *tS* from diverse theoretical methods and from x-ray experiments. The theoretical methods are the present MNDO, AM1, and PM3 calculations, a recent *ab initio*³³ 3-21G study and quantum chemistry force field-configuration interaction (QCFF-CI) study.³² The experimental data are from x-ray diffraction methods using crystal samples.^{14,15}

As we can see from the Table I there is a systematic reduction in the bond lengths from MNDO to PM3; this behavior is also observed for the singlet and triplet calculations in Table III. Of these three methods (MNDO, AM1, and PM3) the PM3 results are closest to the *ab initio* calculation. Considering that the experimental data are for crystal samples and the calculations are for the isolated molecule, the agreement between experiment and theory can be considered very good, although MNDO and QCFF-CI systematically overestimate the bond lengths. The presence of the vinyl group attached to phenyl rings induces only minor distortions ($< 8^\circ$) in the standard 120°

TABLE I. Bond lengths (in angstroms) according to Fig. 1 for planar *trans*-stilbene from MNDO, AM1, PM3, *ab initio*-3-21G, QCFF-CI calculations, and from x-ray diffraction studies (EXP1, EXP2).

	MNDO	AM1	PM3	3-21G ^a	QCFF ^b	Exp1 ^c	Exp2 ^d
C1-C2	1.417	1.402	1.399	1.394	1.422	1.391	1.406
C2-C3	1.406	1.394	1.388	1.380	1.404	1.382	1.393
C3-C4	1.403	1.394	1.391	1.386	1.406	1.376	1.394
C4-C5	1.406	1.395	1.391	1.382	1.406	1.369	1.391
C5-C6	1.403	1.392	1.389	1.383	1.405	1.375	1.390
C6-C1	1.422	1.407	1.399	1.394	1.421	1.379	1.401
C7-C1	1.473	1.453	1.457	1.476	1.477	1.478	1.472
C7-C7'	1.356	1.344	1.342	1.325	1.359	1.300	1.336
C2-H2	1.091	1.100	1.101	1.071		0.94	1.08
C3-H3	1.091	1.100	1.095	1.072		0.98	1.08
C4-H4	1.090	1.099	1.095	1.072		0.98	1.08
C5-H5	1.090	1.100	1.096	1.072		0.96	1.08
C6-H6	1.092	1.100	1.096	1.073		0.95	1.08
C7-H7	1.091	1.105	1.103	1.074		1.02	1.08

^aReference 29.

^bReference 28.

^cReference 11.

^dReference 10.

TABLE II. Bond angle deviations (in degrees) from standard 120.00 value for planar *trans*-stilbene, from MNDO, AM1, PM3, *ab initio* 3-21G, QCFF-CI calculation, and from x-ray diffraction studies (Exp1, Exp2). Numbering follows Fig. 1.

	MNDO	AM1	PM3	3-21G ^a	QCFF ^b	Exp1 ^c	Exp2 ^d
C1-C2-C3	+1.355	+0.555	+0.387	+0.800	+0.700	+0.700	+0.500
C3-C4-C5	+0.426	+0.316	-0.062	-0.600	+0.200	-0.800	-0.700
C4-C5-C6	+0.234	+0.178	+0.259	+0.100	-0.100	+0.500	+0.300
C5-C6-C1	+1.514	+0.659	+0.108	+1.200	+0.400	+1.500	+1.200
C6-C1-C2	-2.830	-1.382	-0.719	-1.900	+0.400	-2.300	-1.900
C7-C1-C6	-2.165	-1.426	-0.321	-1.600	+2.900	-1.900	-1.500
C7'-C7-C1	+8.033	+5.359	+3.082	+6.700	+4.600	+6.600	+6.000
H2-C2-C1	+0.941	+0.247	-0.421	+0.200		-1.500	+0.400
H3-C3-C2	+0.304	+0.207	-0.094	-0.400		-0.100	-0.200
H4-C4-C5	+0.307	+0.134	+0.025	+0.400		+2.300	+0.300
H5-C5-C6	-0.178	-0.134	-0.162	-0.300		-0.600	+0.300
H6-C6-C5	-1.674	-0.268	-0.022	-0.300		+1.010	+0.010
H7-C7-C1	-0.040	-5.741	-2.700	-6.100		+1.100	-2.300

^aReference 29.^bReference 28.^cReference 11.^dReference 10.

value, even in the excited states, as can be seen from Tables II and IV. The electron affinity of *t*S is large, 1.08 eV, and its ionization potential of 8.14 eV is close to the adiabatic gas phase value of 7.66 eV.¹⁸

The x-ray data from crystal samples¹²⁻¹⁶ indicate that *t*S can be considered a coplanar structure with the phenyl rings slightly twisted (3°-7°) with relation to the plane of vinyl group. For the isolated molecule, although there are some gas phase data²² suggesting a large deviation from the planarity (a dihedral angle ~30°), more recent experimental data²³⁻²⁶ clearly indicate a planar geometry in both the ground and singlet excited states.

B. Rotational barriers

We have estimated the energy involved in the rotation of one phenyl ring about the backbone single bond, keeping the remaining structure planar. We show in Fig. 2 the results obtained from MNDO, AM1, and PM3 calculations. Using a frozen or relaxed geometry does not change the general shape of the curve, as shown for the PM3

calculations. We have observed an average reduction of 10% for the 90° value comparing frozen and relaxed geometries. As we can see from Fig. 2, MNDO presents a pathological behavior suggesting a structure very far from planarity. PM3 and AM1 show similar curves, but PM3 indicates a planar structure as the most stable configuration, in accordance with experimental data.²³⁻²⁶ These results are in qualitative agreement with recent *ab initio* calculations;³³ PM3 and AM1 both show the same tendency of underestimating the 90° barrier. But PM3 is actually in better agreement with experimental data leading to a rotational barrier¹⁸ of 1 kcal/mol for the ground state. Although the rotation potential curves show different shape for the three methods, the behavior of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level positions as a function of the angle rotation is very similar, as we can see from Fig. 3.

Based on the above data for geometry and rotational

TABLE III. Bond lengths (in angstroms) for planar *trans*-stilbene in its excited singlet (*S*) and triplet (*T*) states, from MNDO (MN), AM1 (AM), and PM3 (PM) calculations. For comparison the singlet QCFF-CI(QF) results (Ref. 28) are also shown. Numbering follows Fig. 1.

	<i>S</i> -MN	<i>S</i> -AM	<i>S</i> -PM	<i>S</i> -QF	<i>T</i> -MN	<i>T</i> -AM	<i>T</i> -PM
C1-C2	1.432	1.418	1.416	1.448	1.447	1.429	1.427
C2-C3	1.407	1.393	1.389	1.390	1.393	1.382	1.377
C3-C4	1.401	1.391	1.387	1.412	1.410	1.399	1.396
C4-C5	1.414	1.403	1.401	1.419	1.412	1.401	1.397
C5-C6	1.394	1.382	1.379	1.395	1.390	1.379	1.377
C6-C1	1.439	1.423	1.418	1.450	1.453	1.435	1.428
C7-C1	1.437	1.416	1.415	1.424	1.396	1.382	1.381
C7-C7'	1.409	1.396	1.402	1.435	1.467	1.446	1.457
C2-H2	1.089	1.098	1.100		1.090	1.099	1.090
C3-H3	1.091	1.101	1.095		1.091	1.101	1.091
C4-H4	1.090	1.099	1.095		1.089	1.099	1.089
C5-H5	1.091	1.100	1.095		1.091	1.101	1.091
C6-H6	1.094	1.100	1.096		1.091	1.100	1.091
C7-H7	1.094	1.102	1.101		1.094	1.102	1.094

TABLE IV. Bond angle deviations (in degrees) from standard 120.00 value for planar *trans*-stilbene in its excited singlet (*S*) and triplet (*T*) states, from MNDO (MN), AM1 (AM), and PM3 (PM) calculations. For comparison the singlet QCFF-CI(QF) (Ref. 28) results are also shown. Numbering follows Fig. 1.

	<i>S</i> -MN	<i>S</i> -AM	<i>S</i> -PM	<i>S</i> -QF	<i>T</i> -MN	<i>T</i> -AM	<i>T</i> -PM
C1-C2-C3	1.188	0.413	0.225	0.600	1.723	0.957	0.689
C3-C4-C5	0.403	0.307	0.317	0.500	-0.567	0.725	0.276
C4-C5-C6	0.428	0.387	0.479	0.100	0.547	0.505	0.552
C5-C6-C1	1.521	0.749	0.204	0.600	1.917	1.124	0.502
C6-C1-C2	-3.729	-1.948	-1.347	0.200	-4.385	-2.986	-2.120
C7-C1-C6	-0.708	-0.865	0.091	3.000	-0.666	-0.829	0.159
C7'-C7-C1	6.814	3.940	1.814	4.000	7.777	4.732	2.492
H2-C2-C1	0.946	0.703	-1.164		-0.007	-0.585	-1.816
H3-C3-C2	-0.238	-0.307	-0.334		0.102	-0.201	-0.569
H4-C4-C5	-0.007	-0.164	-0.291		0.261	0.119	0.262
H5-C5-C6	0.056	0.140	0.079		-0.003	0.056	-0.003
H6-C6-C5	-1.112	0.306	0.475		-1.015	0.392	-0.902
H7-C7-C1	-4.886	-3.507	-0.798		-3.343	-2.008	-3.343

potential curves, we can conclude that PM3 provides better results than AM1.

C. Excited state geometries

In Tables V and VI we show the PM3 bond lengths and bond angles for the planar *tS* in its ground, excited, and ionic states. As can be seen from the tables, the phenyl rings change from benzenoid to quinoid structure in excited and ionic states, with a reversal of single and double bond in the vinyl group. We note that the modifications induced in the geometry show a similarity between singlet (*S*) and polarons (P^{\pm}), and between triplet (*T*) and bipolarons (B^{\pm}). The tendency of reversing double and single bonds in the vinyl group implies that the phenyl ring rotation shown in Fig. 1 is now about a bond that has some double bond character. The higher energy for rotation about a partial double bond is clearly seen in Fig. 4, which

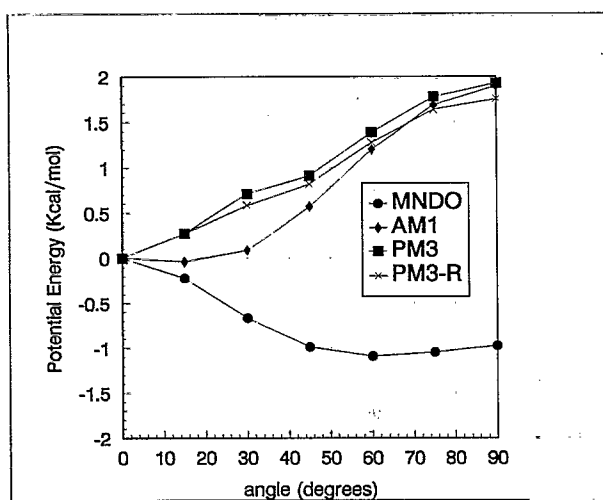


FIG. 2. *trans*-stilbene potential energy curves associated with the rotation about the backbone single bond, keeping the remaining structure planar. MNDO, AM1, and PM3 curves from frozen geometry calculations; PM3-R for relaxed geometry. All energies are relative to the coplanar conformation.

compares the rotational potentials for singlet, triplet, polarons, and bipolarons to the ground state. The slope of the potentials at 90° reflects the unrelaxed geometries. Thus, the process of doping of long PPV oligomers, creating polarons and bipolarons, increases the PPV conductivity not only by creating new charge carriers but also by making the observed ring rotation motions^{10,11} more difficult, thus resulting in increased effective conjugation length.

D. Excitation energies

The heat of formation of polarons and bipolarons with relation to the ground state value suggest that *tS* is a good electron acceptor; there is an energy gain of ~1.1 eV with the capture of one electron, in agreement with experimental data.^{2,3,12} The heats of formation also suggest that negative polarons and bipolarons are more stable than their positive forms.

Although there are many theoretical papers on the ground state of *tS*, there are only few on its excited states.^{30,32,34,35} As we can see from Tables III and IV there

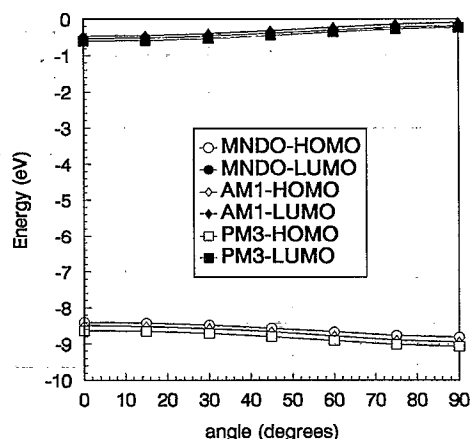


FIG. 3. MNDO, AM1, and PM3 HOMO and LUMO energy positions as a function of ring rotation about the single bond.

TABLE V. Bond lengths (in angstroms) for planar *trans*-stilbene from PM3 calculations in its ground state (*G*), excited states, singlet (*S*) and triplet (*T*), and charged states +1, -1, +2, -2 (positive and negative polarons and bipolarons, P^+ , P^- , B^+ , B^- , respectively). Also indicated is the heat of formation (H.F.) in kcal/mol for each structure relative to the ground state value. Numbering follows Fig. 1.

	<i>G</i>	<i>S</i>	<i>T</i>	P^+	P^-	B^+	B^-
C1-C2	1.399	1.416	1.427	1.420	1.417	1.451	1.446
C2-C3	1.388	1.389	1.377	1.380	1.379	1.366	1.365
C3-C4	1.391	1.388	1.396	1.399	1.394	1.415	1.406
C4-C5	1.391	1.401	1.397	1.397	1.394	1.409	1.401
C5-C6	1.389	1.379	1.377	1.382	1.381	1.371	1.369
C6-C1	1.399	1.418	1.428	1.419	1.417	1.453	1.445
C7-C1	1.457	1.415	1.381	1.412	1.412	1.367	1.367
C7-C7'	1.342	1.402	1.457	1.397	1.388	1.455	1.440
C2-H2	1.101	1.100	1.090	1.102	1.099	1.104	1.098
C3-H3	1.095	1.095	1.091	1.097	1.094	1.103	1.095
C4-H4	1.095	1.095	1.089	1.098	1.092	1.102	1.089
C5-H5	1.095	1.095	1.091	1.098	1.094	1.103	1.096
C6-H6	1.096	1.096	1.091	1.098	1.094	1.101	1.093
C7-H7	1.103	1.101	1.094	1.107	1.100	1.110	1.099
H.F.	...	93.313	46.376	187.667	-24.985	461.486	37.524

is a general agreement between PM3 and QCFF-CI results for the singlet state, although the phenyl ring distortions induced by the transition are more localized (practically only bonds 1-2 and 1-6 are affected) in the PM3 case. These distortions in the phenyl and vinyl groups seem to be consistent with the observed vibrational activity in the singlet spectrum^{18,25} and with recent electronic hyperpolarizability measurements in solution.⁴⁹ However these distortions seem to be overestimated when compared with x-ray data.¹²

One interesting result from PM3 calculations is to look at the differences in the heats of formation values instead of the typically enormous HOMO-LUMO splitting in Fig. 3. The calculated values for the singlet and triplet excitation are 4.05 and 2.01, respectively and the experimental values are 3.997 and 2.13 eV.^{12,25,26} These numbers are also in good agreement with vertical VB-PPP (full CI) excitations, 4.381 and 2.519 eV,^{34,35} respectively. The close agreement of a valence-electron calculation with experiment and full CI for π -electrons is nevertheless unexpected. The PM3 results are for single Slater determinants,

without CI. We have focused on states that are well represented by a single determinant and that have the lowest energy in subspaces with fixed charge, spin or symmetry. Electron-electron correlations are then relatively less important. The reorganization of the ground-state molecular orbitals through separate self-consistent field (SCF) calculations effectively includes some CI in the frozen orbital basis, but we should not expect the same good performance for higher excited states. The generality of this procedure remains to be clarified. At least some excited states, however, may be accessible through separate SCF calculations for all valence electrons rather than restricted CI, and these states include bipolarons.

IV. SUMMARY AND CONCLUSIONS

We have performed a comparative MNDO, AM1, and PM3 study of *trans*-stilbene (*tS*) in its ground, excited (singlet and triplet), and charged (positive and negative polarons and bipolarons) states. Comparison with the available experimental data and other theoretical calcula-

TABLE VI. Bond angles deviations (in degrees) from standard 120.00 value for planar *trans*-stilbene from PM3 calculations in its ground state (*G*), excited singlet (*S*) and triplet (*T*) states, and charged states +1, -1, +2, -2 (positive and negative polarons and bipolarons, P^+ , P^- , B^+ , B^- , respectively). Numbering follows Fig. 1.

	<i>G</i>	<i>S</i>	<i>T</i>	P^+	P^-	B^+	B^-
C1-C2-C3	+0.387	+0.225	+0.689	+0.370	+0.930	+0.627	+1.582
C3-C4-C5	-0.062	+0.317	+0.276	+0.048	-0.686	+0.071	-1.948
C4-C5-C6	+0.259	+0.479	+0.552	+0.324	+0.799	+0.733	+1.911
C5-C6-C1	+0.108	+0.204	+0.502	+0.093	+0.729	+0.263	+1.299
C6-C1-C2	-0.719	-1.347	-2.120	-1.224	-2.428	-2.370	-4.539
C7-C1-C6	-0.321	+0.091	+0.159	-0.475	+0.608	-0.231	+1.641
C7'-C7-C1	+3.082	+1.814	+2.492	+2.885	+3.430	+3.166	+4.395
H2-C2-C1	-0.421	-1.164	-1.816	-1.378	-2.530	-2.104	-3.833
H3-C3-C2	-0.094	-0.334	-0.569	+0.164	-0.501	+0.425	-1.527
H4-C4-C5	+0.025	-0.291	+0.262	-0.135	+0.337	-0.019	+1.059
H5-C5-C6	-0.162	+0.079	-0.003	+0.011	-0.201	+0.087	-0.401
H6-C6-C5	-0.022	+0.425	-0.902	+0.175	-1.008	+0.693	-1.943
H7-C7-C1	-2.700	-0.798	-3.343	-1.180	-1.298	+0.339	-0.037

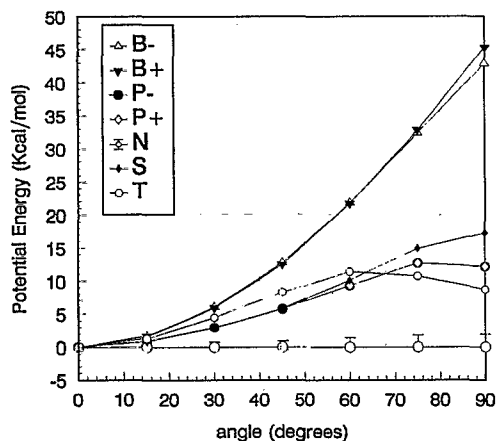


FIG. 4. PM3 potential energy curves for the ground (*N*), singlet (*S*), triplet (*T*), positive and negative polarons (*P*), and bipolarons (*B*) states. All energies are given with relation to the coplanar configuration.

tions show that PM3 is superior to MNDO and AM1. The PM3 heats of formation predict observed singlet and triplet excitations surprisingly well. Further studies are required to clarify these aspects.

PM3 predicts, in contrast with MNDO, AM1 and even *ab initio* 3-21G,³³ a planar conformation for the ground *tS* state, in accordance with recent experimental data.³² PM3 also predicts a low barrier for ring rotation about backbone single bonds in the ground state, with the barrier increasing in the following order: triplet, polarons, singlet, and bipolarons. Increasing the barrier for excited and ionic states (Fig. 4) makes these ring rotations more difficult. We anticipate that doping long PPV oligomers increases the conductivity not merely by increasing the number of charge carriers, but also by increasing the effective conjugation length, as a consequence of increased barrier to ring rotations.^{10,11}

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