

Density-functional crystal orbital study on the structures and energetics of polyacetylene isomers

So Hirata

The Graduate University for Advanced Studies and Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan

Hajime Torii

Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

Mitsuo Tasumi*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan

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Total energies and optimized molecular structures of the *trans-transoid* (Tt) and *cis-transoid* (Ct) forms of polyacetylene are calculated by the density-functional crystal orbital method. The Slater-Vosko-Wilk-Nusair (SVWN), the Becke-Lee-Yang-Parr (BLYP), and the Becke3-Lee-Yang-Parr (B3LYP) functionals are used with the 3-21G and 6-31G* basis sets. Potential-energy curves of the Ct form along the bond-alternation coordinate [which represents the transition from the Ct form to the *trans-cisoid* (Tc) form] are calculated with the SVWN, BLYP, and B3LYP functionals. The SVWN and BLYP functionals seriously underestimate the double-minimum character of the potential-energy curves, so that the calculated potential-energy curves have no local minimum at the Tc structure. The potential-energy curves calculated with the B3LYP functional have distinct shoulders at the Tc structure, and the structural parameters of the Tc form are optimized with this functional. The structural parameters and ultraviolet photoelectron spectra of the Tt and Ct forms calculated by using the B3LYP functional are in reasonable agreement with the experimental results. Potential-energy curves along the CC-CC dihedral angle coordinate are calculated with the B3LYP functional. It is found that the calculated potential-energy curve has a shallow local minimum at the *cis-gauche* (Cg) form. The B3LYP functional predicts the total energies of the polyacetylene isomers increase in the order $Tt < Ct < Tc < Cg$. [S0163-1829(98)12019-2]

I. INTRODUCTION

Density-functional theory has been extensively used for the calculations of energetics, structures, and vibrations of molecular systems.^{1,2} This is because density-functional calculations can include electron correlation with relatively small computational costs, which are in the same order of magnitude as the costs needed for Hartree-Fock (HF) calculations. Density-functional theory is applicable to relatively large systems for which HF-based correlated calculations are not feasible.

It is therefore natural to adopt density-functional theory for the description of the electronic and structural properties of conjugated π -electron polymers, for which the effect of electron correlation is essential. Among these conjugated π -electron polymers, polyacetylene³ is the most frequently studied material because of its intriguing electrical and spectroscopic behavior. There have been a number of density-functional studies on polyacetylene.⁴⁻¹⁵ Suhai¹⁵ has recently published a paper in which the bond alternation in the *trans-transoid* (Tt) form of polyacetylene is thoroughly investigated with various exchange-correlation functionals. Suhai has found that the magnitude of the bond alternation in the Tt form is reasonably predicted when functionals mixed with exact exchange are used.

Although the electronic and structural properties of Tt polyacetylene have been repeatedly investigated, studies on the other geometric isomers, namely, the *cis-transoid* (Ct), *trans-cisoid* (Tc), and *cis-gauche* (Cg) (Ref. 16) forms, are

not abundant. The structures of these four isomers are shown in Fig. 1. It is not only of interest but also of importance to study the structures and energetics of these isomers at an equal theoretical level, which takes the effect of electron correlation into account.

In this paper, we present the total energies and optimized

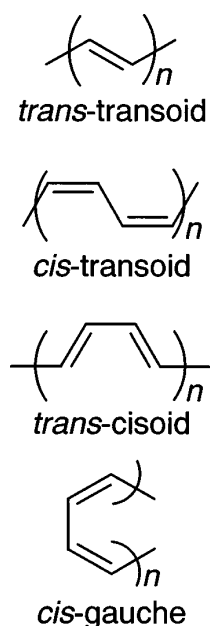


FIG. 1. Isomers of polyacetylene.

molecular structures of the Tt and Ct forms of polyacetylene obtained from density-functional crystal orbital calculations. The local Slater-Vosko-Wilk-Nusair (SVWN), the gradient-corrected Becke-Lee-Yang-Parr (BLYP), and the hybrid Becke3-Lee-Yang-Parr (B3LYP) functionals are used in combination with the standard 3-21G and 6-31G* basis sets. The role of the exact-exchange mixing in determining the shape of the potential-energy curves along the bond-alternation coordinate is discussed. The ultraviolet photoelectron spectra calculated with the B3LYP functional are compared with the experimental results for the Tt and Ct forms. Structures and energetics of the Tc and Cg forms are also examined with the B3LYP functional. The relative energies of the four forms of polyacetylene are discussed.

II. METHOD OF CALCULATION

The density-functional crystal orbital method for helical polymers is a straightforward combination of the HF crystal orbital method¹⁷⁻²¹ and the molecular density-functional method,^{22,23} so its formulation is not presented here. In this section, only the computer implementation of the method is described.

We employed the Gaussian basis sets for the expansion of Kohn-Sham orbitals, and hence, the overlap integrals, kinetic energy integrals, and nuclear attraction integrals were analytically evaluated by the Obara-Saika recursion formula.²⁴ Electron density was also expanded by sets of Gaussian functions (hereafter referred to as the auxiliary basis sets), so that the Coulomb matrix elements were calculated by the two- and three-index electron repulsion integrals. These integrals were analytically evaluated by the Obara-Saika recursion scheme reformulated by Andzelm and Wimmer²⁵ for the computation of the two- and three-index electron repulsion integrals. The expansion of electron density was based on the method of Dunlap, Connolly, and Sabin,²⁶ which was previously adopted by Mintmire and White^{6,8} for the $X\alpha$ calculations of the Tt form of polyacetylene. It should be emphasized that the approximate total Coulomb energy calculated by this method is a variational extremum with respect to the expansion coefficients, and that the errors in the calculated energies introduced in this treatment (estimated to be about 2×10^{-4} a.u. per atom) will almost cancel each other as far as the total energy difference is concerned. The lattice sums used in evaluating the Coulomb matrix elements exhibit slow convergence due to the long-range nature of Coulomb interactions.^{27,28} We calculated these lattice sums by evaluating explicitly the relevant two- and three-index electron repulsion integrals extending to the twentieth neighboring C_2H_2 unit cells within the Namur cutoff procedure.^{29,30} For the other molecular integrals, we took into account the interactions up to the fourth to eighth neighboring C_2H_2 unit cells depending upon the basis set used and upon the translational period of the system.

The exchange-correlation integrals were computed numerically by the method developed by Becke³¹ applying a second-kind Gauss-Chebyshev quadrature for the radial integration and a Lebedev quadrature³²⁻³⁴ for the angular integration. The numerical grid consisted of 50 radial points and 302 angular points. Smaller angular grids were used for radial shells close to the nuclei (38-point angular grid for radial

TABLE I. Exponents of the auxiliary Gaussian functions for hydrogen and carbon.

Auxiliary basis set I		Auxiliary basis set II	
Hydrogen	Carbon	Hydrogen	Carbon
	<i>s</i>		<i>s</i>
10.89	344.5	37.46	512.6
3.298	99.63	21.56	170.9
	33.21	19.37	56.95
	11.07	18.89	18.98
		5.651	15.74
		3.466	10.80
		2.987	6.328
			5.399
	<i>spd</i>		<i>spd</i>
1.099	7.330	1.280	2.699
0.3664	3.525	0.8014	
	1.175		<i>spdf</i>
	0.3917	0.3226	1.350
			0.6749
			0.3374

shells 1–12 and 50-point angular grid for radial shells 13–25) and the $M4$ mapping of radial grid points was adopted according to the recommendation of Treutler and Ahlrichs.³⁵ The resulting 8656-point grid was used for carbon and hydrogen, and an error in the integrated electron density of polyacetylene was typically 1×10^{-5} per atom.

We employed the standard 3-21G (Ref. 36) and 6-31G* (Refs. 37 and 38) basis sets for the expansion of Kohn-Sham orbitals and 201 evenly spaced wave vectors to describe the first Brillouin zone. It has been pointed out^{8,11,14} that a sufficiently large number of wave vectors are necessary to accurately evaluate the magnitude of bond alternation in the Tt form of polyacetylene. Two sets of auxiliary basis functions were employed: auxiliary basis set I for the 3-21G calculations and auxiliary basis set II for the 6-31G* calculations. Auxiliary basis set I consisted of uncontracted s -type Gaussian functions and blocks of uncontracted s -type, p -type, and d -type Gaussian functions with shared exponents. Auxiliary basis set II consisted of uncontracted s -type, p -type, d -type, and f -type Gaussian functions, some of which have shared exponents. The exponents of the auxiliary basis functions are given in Table I. Since the convergence of the lattice sums for the exact-exchange matrix elements is generally much faster than that for the Coulomb matrix elements,²¹ the four-index electron repulsion integrals, which were necessary to compute the exact-exchange matrix elements, were explicitly evaluated by using the Obara-Saika recursion formula. In the present study, the Slater local exchange,³⁹ the Vosko-Wilk-Nusair local correlation,⁴⁰ the Becke gradient-corrected exchange,⁴¹ and the Lee-Yang-Parr gradient-corrected correlation^{42,43} functionals were used. The effect of the exact-exchange mixing was examined with the B3LYP functional.⁴⁴ These three exchange-correlation functionals have been widely used in molecular applications, and the performance of these functionals for predicting thermochemical quantities,^{23,25,44–49,51,52} equilibrium

TABLE II. Optimized structural parameters of polyacetylene in units of Å (bond length) and degrees (bond angle).

Structural parameter	SVWN		BLYP		B3LYP	
	3-21G	6-31G*	3-21G	6-31G*	3-21G	6-31G*
	<i>trans-transoid</i>					
C=C bond length	1.383	1.384	1.404	1.398	1.366	1.369
C—C bond length	1.395	1.392	1.410	1.413	1.428	1.426
C—H bond length	1.101	1.102	1.097	1.099	1.090	1.091
CCC angle	124.2	124.3	124.3	124.6	124.3	124.5
C=CH angle	118.0	117.9	117.9	117.9	118.5	118.3
	<i>cis-transoid</i>					
C=C bond length	1.372	1.375	1.388	1.390	1.366	1.369
C—C bond length	1.414	1.412	1.435	1.433	1.438	1.435
C—H bond length	1.098	1.099	1.093	1.095	1.086	1.087
CCC angle	125.9	126.0	126.6	127.0	126.5	126.7
C=CH angle	117.0	116.9	116.3	116.1	116.7	116.4
	<i>trans-cisoid</i>					
C=C bond length	a	a	a	a	1.373	b
C—C bond length					1.429	
C—H bond length					1.087	
CCC angle					126.9	
C=CH angle					117.9	

^aNo local minimum corresponding to the *trans-cisoid* form was found with the SVWN and BLYP functionals.

^bSee text.

structures,^{23,25,49,50,52} and harmonic vibrational frequencies^{23,25,49,52–54} has been investigated.

The direct inversion in the iterative subspace (DIIS) extrapolation⁵⁵ was employed for the convergence acceleration of the self-consistent-field iteration. The criterion for the convergence of the density matrix elements was set to 10^{-6} . The geometry optimization was performed by Powell's conjugate direction method,⁵⁶ in which the minimization along each conjugate direction was based on the three-point parabolic interpolation. As far as the numerical accuracy in the present optimization method is concerned, the bond lengths (in Å) are accurate to three decimal places and bond angles (in degrees) are accurate to one decimal place.

III. RESULTS AND DISCUSSION

Optimized structural parameters for the Tt and Ct forms of polyacetylene obtained with the SVWN, BLYP, and B3LYP functionals are shown in Table II. Structure is optimized also for the Tc form at the B3LYP/3-21G level. In the present geometry optimization, the planarity of the polyacetylene molecule was assumed, and all the remaining structural parameters were optimized. The assumption of planarity of the molecule is partially supported by the results of the present study, where the potential energies are plotted along the CC-CC dihedral angle (see below), and by the results of the vibrational analyses of the polyacetylene isomers.^{57–59}

The magnitude of the bond alternation (hereafter designated as Δr) in the Tt form calculated at the SVWN/3-21G and SVWN/6-31G* levels are 0.012 and 0.008 Å, respectively, and are much smaller than the experimental value

(0.08 Å).⁶⁰ It has already been reported^{8,10–12,14} that the calculated values of Δr tend to be too small in the framework of the local-density approximation. Suhai¹⁵ has analyzed the effects of the gradient correction and the exact-exchange mixing on the calculated value of Δr . He has found that the situation is hardly improved by the gradient correction, but the mixing of exact exchange at the Becke-half-and-half-Lee-Yang-Parr level yields a reasonable value for Δr . In the present study also, the values of Δr calculated at the BLYP/3-21G and BLYP/6-31G* levels (0.006 and 0.015 Å, respectively) are too small, but the values obtained with the B3LYP functional seems to be reasonable. The C=C and C—C bond lengths calculated at the B3LYP/3-21G level (1.366 and 1.428 Å, respectively) and at the B3LYP/6-31G* level (1.369 and 1.426 Å, respectively) are consistent with the values obtained experimentally (1.36 ± 0.01 and 1.44 ± 0.01 Å, respectively).⁶⁰ The structural parameters calculated at the B3LYP/6-31G* level are close to those obtained at the B3LYP/3-21G level and hence, the basis-set dependence of the structural parameters is not prominent for this system.

For the Ct form, the calculated C=C and C—C bond lengths are significantly different from each other with all the functionals used. This result is reasonable in view of the geometrical nonequivalence of the adjacent CC bonds in the Ct form. However, the shape of the potential-energy curve along the bond-alternation coordinate is strongly affected by the mixing of exact exchange not only for the Tt form but also for the Ct form. The potential-energy curves of the Ct form along the bond-alternation coordinate Δr (which represents the transition from the Ct form to the Tc form) are

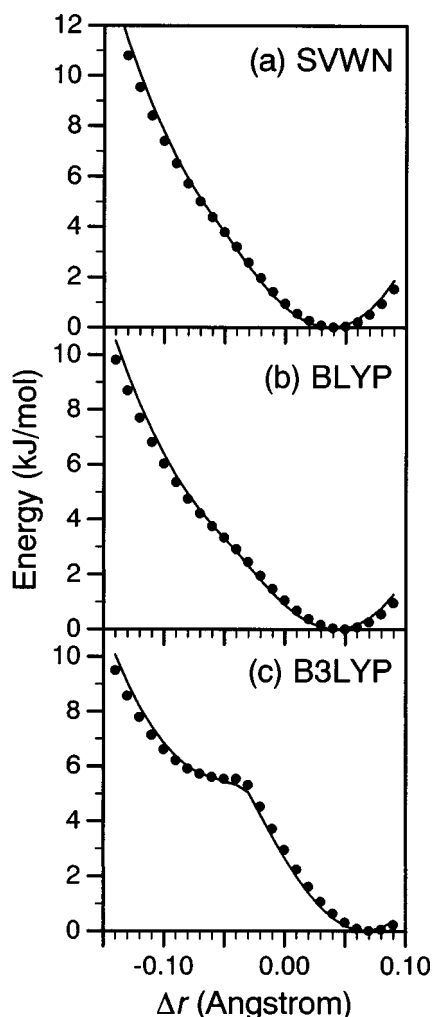


FIG. 2. Energy per C_2H_2 unit of the *cis-transoid* (*trans-cisoid*) form of polyacetylene calculated with the (a) SVWN, (b) BLYP, and (c) B3LYP functionals as a function of the degree of bond alternation (Δr). The results obtained with the 3-21G basis set are represented by filled circles, and those obtained with the 6-31G* basis set by solid curves. Energy is zero for the *cis-transoid* form. The C—H bond length, CCC angle, C=CH angle, and the sum of the C=C and C—C bond lengths are fixed at the optimized values for the *cis-transoid* form.

shown in Fig. 2, with the sign of Δr being taken to be positive for the Ct structure. The curves obtained with the 6-31G* basis set overlap with those obtained with the 3-21G basis set, indicating that the basis-set dependence on the potential-energy curves along Δr is again small regardless of the exchange-correlation functionals used. The small basis-set dependence is expected since the total energies of the structures with different values of Δr are lowered by a similar amount by augmenting the basis set. With the SVWN and BLYP functionals, the potential-energy curves deviate only slightly from the harmonic shape around the region $\Delta r \approx -0.05$ Å where the local minimum corresponding to the Tc form is expected to appear. When the B3LYP functional is used, a distinct shoulder or minimum appears at $\Delta r \approx -0.05$ Å. The curve obtained at the B3LYP/3-21G level has a shallow local minimum at $\Delta r \approx -0.05$ Å, which corresponds to the Tc form. The potential energy curve calculated at the B3LYP/6-31G* level, on the other hand, does

not have a local minimum at the Tc structure. Since the structural parameters are not optimized at each value of Δr , the present result does not necessarily rule out the existence of the local minimum of the Tc form at the B3LYP/6-31G* level. However, no attempt was made to locate the local minimum of the Tc form at the B3LYP/6-31G* level, because the convergence of the self-consistent field procedure is much slower in this Δr region, probably due to the small HOMO-LUMO band gap, than in the other region. Figure 2(c) suggests that the energy barrier for the Tc→Ct isomerization is very low and the Tc isomer can easily isomerize to the Ct isomer by interchanging the C=C and C—C bond lengths even if a local minimum exists for the Tc form. It should be remembered that Tc polyacetylene has not been experimentally detected as a stable isomer.

The magnitude of the bond alternation in the Ct form calculated with the SVWN and BLYP functionals are in the range of 0.03–0.05 Å, and are smaller than the value obtained with the B3LYP functional (about 0.07 Å). It is considered that the potential energy curves calculated with the SVWN and BLYP functionals tend to have too weak double-minimum character. The too small degree of bond alternation calculated with the SVWN and BLYP functionals for the Tt form suggests that the potential-energy curves calculated with these functionals are not satisfactory also for the Ct form. It should also be added that the B3LYP calculations reproduced the frequencies of the infrared- and Raman-active vibrations of the Tt and Ct forms with considerable accuracy.⁵⁹ It is therefore considered that the potential-energy curves calculated with the B3LYP functional are reasonable.

In our previous study,⁵⁸ the structural parameters of the Ct and Tc forms were extrapolated from those of the Ct and Tc oligoenes calculated at the B3LYP/6-31G* level. Although the structural parameters of the Ct form obtained by extrapolation are not far from the result of the present study, the C=C and C—C bond lengths obtained by extrapolation (1.374 and 1.429 Å, respectively) differ from the values obtained in the present study (1.369 and 1.435 Å, respectively). These differences are due to the overestimation of the chain-length dependence of the C=C and C—C bond lengths in the extrapolation in our previous study.⁵⁸ Nevertheless, the C=C bond lengths calculated by either of the above two methods are within the error of the experimental value (1.37 ± 0.01 Å).⁶⁰

A number of density-functional studies have analyzed the conformation and internal rotation potential about the C—C bonds in conjugated and nonconjugated molecules.^{61–67} These studies have demonstrated that the relative energies of conformers predicted by density-functional theory are generally in good agreement with the experimental results and with the results obtained by high-level *ab initio* molecular orbital calculations, except for the recent study of Choi, Kertesz, and Karpfen⁶⁷ (see below). In what follows, the relative stability and internal rotation potentials of the polyacetylene isomers are examined by the use of the B3LYP functional.

The total and relative energies of the three forms of polyacetylene at their optimized structures are shown in Table III. With all the functionals used, the relative stability of the Tt and Ct forms is predicted in the order expected from experi-

TABLE III. Calculated total and relative energies of polyacetylene. Total energies (E) in atomic units per C_2H_2 unit, and energies relative to the *trans*-*transoid* form (ΔE) in kJ mol^{-1} per C_2H_2 unit.

Functional/ basis set	<i>trans</i> - <i>transoid</i>		<i>cis</i> - <i>transoid</i>		<i>trans</i> - <i>cisoid</i>	
	E	ΔE	E	ΔE	E	ΔE
SVWN/3-21G	-76.543 05	0.0	-76.540 10	7.7	a	
SVWN/6-31G*	-76.963 14	0.0	-76.959 57	9.4	a	
BLYP/3-21G	-76.946 59	0.0	-76.942 96	9.5	a	
BLYP/6-31G*	-77.371 23	0.0	-77.367 08	10.9	a	
B3LYP/3-21G	-76.983 39	0.0	-76.980 17	8.5	-76.978 24	13.5
B3LYP/6-31G*	-77.407 82	0.0	-77.404 08	9.8	b	

^aNo local minimum corresponding to the *trans*-*cisoid* form was found with the SVWN and BLYP functionals.

^bSee text.

ment. The relative energies of the Ct and Tc forms calculated at the B3LYP/3-21G level are 8.5 and 13.5 kJ mol^{-1} , respectively. These values are comparable to those obtained at the HF/4-31G level (8.7 and 15.0 kJ mol^{-1} , respectively).²⁸ The relative energy of the Ct form calculated at the B3LYP/6-31G* level is 9.8 kJ mol^{-1} and is consistent with the result of our previous calculations on oligoenes at the B3LYP/6-31G* level (for example, the corresponding relative energy is 6.4 kJ mol^{-1} for 1,3,5,7,9,11,13-tetradecaheptaene and is expected to increase with increasing chain length).⁵⁸ The present result, on the other hand, disagrees with the result of a previous linear-muffin-tin-orbital local-density functional study,⁷ which predicted that the Tc form was more stable than the Ct form.

The energies of the various forms of polyacetylene calculated with the B3LYP functional are plotted as a function of the CC-CC dihedral angle in Fig. 3. The plot in Fig. 3(a) was obtained by changing the dihedral angle alone with all the remaining structural parameters fixed at the optimized values of the Tt form. The filled circles represent the results obtained at the B3LYP/3-21G level and the solid curves represent those obtained at the B3LYP/6-31G* level. The filled circles and solid curves in Fig. 3(b) were likewise drawn by fixing all the structural parameters other than the CC-CC dihedral angle at the optimized values of the Ct form.

The potential-energy curve in Fig. 3(a) has minima at the dihedral angles of 0° and 180° corresponding to the Tc and Tt forms, respectively. The calculated potential energy curve suggests that the Tc form as well as the Tt form has a planar structure. The same conclusion has been drawn by Teramae, Yamabe, and Imamura⁶⁸ on the basis of the vibrational analysis of the Tc form at the HF/STO-3G level. The potential-energy curve calculated with the 6-31G* basis set has a slightly higher energy barrier at about 100° than that calculated with the 3-21G basis set.

The potential-energy curves in Fig. 3(b) have a deep minimum at 180° (Ct form) and a shallow minimum at about 60° . At the latter minimum, the conformation about the C—C bonds is *gauche* rather than *s-cis*. It is therefore more appropriate to call this form *cis-gauche* (Cg) rather than *cis-cisoid* (Cc). The potential-energy curve rises sharply at 45° and reaches infinity at 0° due to steric hindrance. The potential-energy curve obtained with the 3-21G basis set is

almost parallel to that obtained with the 6-31G* basis set, although the use of the 6-31G* basis set slightly raises the internal rotation barrier for Cg→Ct isomerization from 6.9 to 7.7 kJ mol^{-1} . Owing to π -electron conjugation, it is expected that the C=C and C—C bond lengths change significantly with the CC-CC dihedral angle. The potential-energy curve calculated with the 3-21G basis set by optimizing the

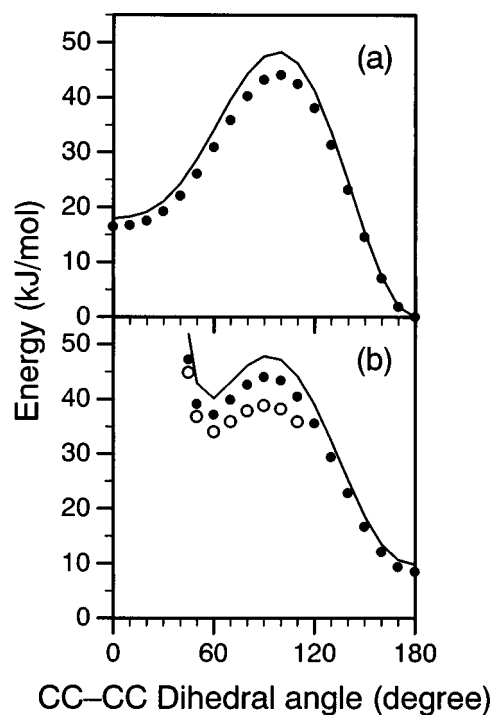


FIG. 3. Energies per C_2H_2 unit of (a) the *trans*-*transoid* (*trans*-*cisoid*) and (b) the *cis*-*transoid* (*cis*-*gauche*) forms of polyacetylene calculated with the B3LYP functional as a function of the CC-CC dihedral angle. The results obtained with the 3-21G basis set are represented by filled circles, and those obtained with the 6-31G* basis set by solid curves. Energy is zero for the *trans*-*transoid* form. Filled circles and solid curves in (a) and (b) are obtained by changing the CC-CC angles with all the other structural parameters fixed at the optimized values of the *trans*-*transoid* and *cis*-*transoid* forms, respectively. Open circles in (b) are plotted by optimizing the C=C and C—C bond lengths for each CC-CC angle by using the 3-21G basis set.

C=C and C—C bond lengths at each fixed dihedral angle is shown in Fig. 3(b) by open circles. For all the dihedral angles investigated, the C—C bond lengths are longer and the C=C bond lengths are shorter than the corresponding optimized values of the Ct form (1.438 and 1.366 Å, respectively). The C—C bond is longest (1.484 Å) at 100°, which is longer than that at 180° (Ct form) by as much as 0.046 Å. This contrasts with nonconjugated systems such as polyethylene, for which the variation in the C—C bond length is 0.02 Å at maximum.⁶⁶ The internal rotation barrier for the Cg→Ct isomerization is lowered from 6.9 to 4.8 kJ mol⁻¹ by taking the structural relaxation into account, but the local minimum still exists at the Cg structure. (The present result does not necessarily mean that polyenes with finite chain lengths can also exist in the Cg structure. For example, geometry optimizations at the B3LYP/3-21G level suggest that 1,3,5,7,9,11-dodecahexaene in the Cg form is unstable along the internal rotation coordinate about the central C—C bond, and 1,3,5,7,9,11,13,15-hexadeca-octaene in the Cg form is unstable along the internal rotation about the C₄—C₅ and C₁₂—C₁₃ bonds.) As a helix, the Cg form has much higher energy than the other forms. The energy difference between the Cg and Tt forms is larger than 30 kJ mol⁻¹. This result is a consequence of the fact that the energy lowering due to the π -electron delocalization is much less in the helical Cg form than in the other planar forms.

The present calculations, therefore, conclude that the total energies of the polyacetylene isomers increase in the order Tt<Ct<Tc<Cg, in accordance with the result of our previous oligomer calculations.⁵⁸ One should also keep in mind that the existence of the local minimum for the Tc form is not confirmed at the B3LYP/6-31G* level. Rather, the B3LYP/6-31G* calculations suggest that the Tc form is unstable toward the formation of the Ct form by interchanging the C=C and C—C bond lengths. This result as well as the predicted order of total energies is consistent with the experimental results that the most stable polyacetylene isomer is the Tt form and the second most stable isomer is the Ct form,⁶⁹ and that the Tc and Cg forms have not been synthesized or detected with confidence. The present result, however, disagrees with the results of previous experimental⁷⁰ and theoretical studies,^{71,72} which suggested that the Cg form might be more stable than the Ct form in solution.

Recently, Choi, Kertesz, and Karpfen⁶⁷ demonstrated that the internal rotation potential about the central C—C bond of 1,3-butadiene calculated by density-functional theory was different from those calculated with the *ab initio* molecular-orbital theory. Internal rotation barrier between the *s-trans* and *gauche* minima predicted by the density-functional theory was higher than those obtained with the HF and second-order Møller-Plesset perturbation (MP2) methods as well as the experimental results. Although the internal rotation potential calculated with the B3LYP functional was found to be in the best agreement with the experimental results among various exchange-correlation functionals examined, there still existed noticeable differences between them.⁶⁷ Choi, Kertesz, and Karpfen suggested that density-functional theory tended to overestimate the barriers for the internal rotation involving partial π -bond breaking. In view of these results, the internal rotation barriers between the Tt and Tc minima and between the Ct and Cg minima calcu-

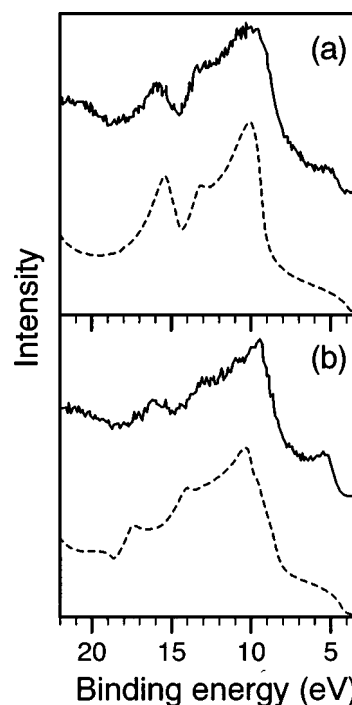


FIG. 4. Calculated (broken curves) and observed (solid curves) ultraviolet photoelectron spectra of (a) the *trans-transoid* and (b) the *cis-transoid* forms of polyacetylene. The observed spectra are taken from Ref. 74.

lated with the B3LYP functional may be overestimated. Since the Cg form has a nonplanar structure with the π -electron conjugation being partially broken, the energy differences between the Cg form and the other three planar forms (Tt, Ct, and Tc) may also be overestimated.

Notwithstanding the above-mentioned limitations, we consider that the order of the total energies of the polyacetylene isomers predicted with the B3LYP functional is reliable, because the B3LYP functional correctly reproduced the order of the total energies of the *s-trans*, *gauche*, and *s-cis* forms of 1,3-butadiene.⁶⁷ Oie, Topol, and Burt⁶⁴ have also found that the energy differences between the conformers of various conjugated molecules obtained by gradient-corrected density-functional theory are in reasonable agreement with the experimental results as well as the results obtained with the MP2 or MP4 calculations.

Crystal-orbital calculations based on density-functional theory are helpful in the interpretation of photoelectron spectra, as has been demonstrated by Springborg and Lev⁷³ and by Miao *et al.*⁶⁶ in the case of polyethylene. In Fig. 4, the calculated ultraviolet photoelectron spectra of the Tt and Ct forms are compared with the observed spectra.⁷⁴ The calculated spectra were obtained by convoluting a band-shape function with the density of states for one-particle orbitals derived from the B3LYP/6-31G* calculations. As the band-shape function, an “asymmetric” Lorentzian function, whose half width at half maximum was 0.25 eV for the low-energy side and 1.35 eV for the high-energy side, was used. The use of the asymmetric function will be justified by the presence of vibronic levels, which is expected to make the band profiles broader in the high-energy side than in the low-energy side. The overall profiles of the calculated spec-

tra are in reasonable agreement with the observed, although the calculated peak positions are slightly higher than those observed for Ct polyacetylene. The agreement is better in the present study than in the previous one⁷⁴ in which the calculated spectra were obtained by convoluting a symmetric band-shape function with the energy levels of oligoenes. The observed spectra of Tt and Ct polyacetylene are similar to each other, but the observed spectrum of Tt polyacetylene is slightly more structured in the 10–20 eV region than that of Ct polyacetylene. The present calculations reproduce this difference in the spectra. This result indicates that the energy-band structures obtained from the B3LYP/6-31G* calculations are sufficiently reliable for the analysis of experimental results, although some ambiguity remains in their physical meaning. The spectra calculated at the B3LYP/3-21G level (not shown) are practically the same as those calculated at the B3LYP/6-31G* level. Thus, the energy-band structures are relatively insensitive to the basis set employed. The use of the SVWN and BLYP functionals also leads to similar spectra for the Tt and Ct forms, except that the peak positions calculated with the SVWN and BLYP functionals are lower than those calculated with the B3LYP functional by about 1 and 2 eV, respectively. However, it does not seem to be appropriate to use the energy-band structures calculated with the SVWN and BLYP functionals in analyzing the experimental data at least for the Tt form, because these two functionals predict too small a band gap for the Tt form. The underestimation of the band gap is closely related to the underestimation of the bond alternation.⁸

IV. SUMMARY AND CONCLUSION

The results of the present study are summarized as follows. (1) The effect of the exact-exchange mixing is substantial on the shape of the potential-energy curves along the bond-alternation coordinate. The SVWN and BLYP functionals tend to underestimate the double-minimum character of the potential-energy curves not only for the Tt form but also for the Ct form of polyacetylene. (2) The optimized structural parameters of the Tt and Ct forms obtained from the B3LYP calculations are reasonable in comparison with the experimental results. (3) The potential-energy curve of the Ct form along the bond-alternation coordinate suggests that the energy barrier for the Tc→Ct isomerization is very low. (4) The B3LYP calculations indicate that the total energies of the Tt, Ct, Tc, and Cg forms increase in this order. (5) The B3LYP calculations satisfactorily reproduce the observed ultraviolet photoelectron spectra of the Tt and Ct forms.

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*Author to whom correspondence should be addressed. FAX: +81-48-858-3379. Electronic address: tasumi@chem.saitama-u.ac.jp

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