

trans-1,2-Dicyano-cyclopropane and other cyano-cyclopropane derivatives

A theoretical and experimental VA, VCD, Raman and ROA spectroscopic study

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Abstract In this work we present the experimental vibrational absorption (VA), vibrational circular dichroism (VCD) and Raman spectra for (+)-*trans*-1(S),2(S)-dicyano-cyclopropane and its dideuterio derivative, *trans*-1(S),2(S)-dicyano-1(S),2(S)-dideuteriocyclopropane, along with VA, VCD, Raman and Raman optical activity (ROA) spectral simulations. Here we investigate the applicability of various local and non-local exchange-correlation (XC) functionals, hybrids and meta-hybrids to reproduce the vibrational

spectra of this strained ring system, which also bears two cyano groups. At the highest level of theory, B3PW91/aug-cc-pVTZ, we also investigated the *trans*-, *cis*- and *gem*-dicyanocyclopropane (*trans*-, *cis*-, and *gem*-DCCP), cyano-cyclopropane (CCP) and the parent molecule cyclopropane (CP). In doing so we have investigated the electronic effects (coupling) between the cyano groups and the cyclopropane ring. In addition to providing an interpretation of the experimentally observed vibrational spectra for these molecules, this work also provides benchmark calculations for other methods, especially semi-empirical based wave function and density functional theory (DFT) based methods, such as SCC-DFTB and PM6. For the semi-empirical DFT based methods to be used for 3-membered ring systems, one ought to document their reliability for systems which were not used in the parameterization. The small 3- and 4-membered ring systems are good test systems because they contain non-standard bonding, which may be difficult to determine accurately with the approximations used in the SCC-DFTB and other semi-empirical methods. Like molecular mechanics force fields, semi-empirical methods, based on DFT and wave function quantum mechanics (WFQM), must be benchmarked against high level *ab initio* and DFT calculations and experimental data. In addition to bonding, the changes in the electric dipole moment, magnetic dipole moment, electric dipole-electric dipole polarizability, electric dipole-magnetic dipole polarizability and electric dipole-electric quadrupole polarizability with respect to nuclear displacement and nuclear velocity can be determined by the VA, VCD, Raman and ROA intensities. Hence it is important that the semi-empirical based DFT and wave function methods not only be parameterized to determine energies, gradients and Hessians, but also the electric and magnetic moments and their derivatives that determine the electronic and magnetic properties of these molecules and their interactions with matter and radiation. This will

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allow biochemists, biophysicists, molecular biologists, and physical biologists to use experimental and theoretical VA, VCD, Raman and ROA spectroscopies to probe biophysical and biochemical function and processes at the molecular level.

Keywords Conformational analysis · Vibrational spectroscopy · VA · VCD · Raman and ROA · DFT · SIESTA · CADPAC · PBE · PBE0 · BP91 · BLYP · B3LYP

1 Introduction

Previously we have presented our preliminary works on *trans*-1,2-dicyanocyclopropane [1–5]. Additionally the vibrational absorption (VA) spectra of both *cis*- and *trans*-dicyanocyclopropane (*cis*- and *trans*-DCCP) have been investigated [6]. *trans*-DCCP is an interesting molecule as a result of its unique bonding and electronic properties due to the strained 3-membered cyclopropane (CP) ring. Many studies have been made on the parent molecule and also various derivatives, for example, *trans*-1,2-dimethylcyclopropane, which is chiral. In this work we investigate the cyano derivatives to determine the structural, electronic, and magnetic properties of this system, as well as the substituent effects. In our more recent works we have used VA, vibrational circular dichroism (VCD), Raman, and Raman optical activity (ROA) spectroscopic methods to answer structural questions in a variety of biologically relevant molecules; L-alanine (LA) [7–11], *N*-acetyl L-alanyl *N*'-methylamide (NALANMA) [7, 11–15], L-histidine [16], L-alanyl L-alanine (LALA) [7, 17, 18], 3-methylindole [19], tri-L-serine [20, 21], phenylloxirane [22], *N*-acetyl tri-L-serine *N*'-methyl-amide [20] and Leu-enkephalin [23]. Combined conformational and vibrational analysis of free 12-crown-4 and its alkali metal complexes led to the prediction of the conformation in which these molecules exist [24–27]. In these works the influence of the environment was shown to be very important. This was due in part to the inherent flexibility in these molecules, and/or the aqueous environments for relevant experimental data. In contrast, more rigid, hydrophobic molecules, such as aframodial [28], typically afford a good ability to compare ostensibly gas phase calculations to experimental data in generally non-interacting organic solvents. This applies for the current set of small 3-membered ring cyclic structures. Given the small size, absence of conformational flexibility, and explicit solvent dependence, CP and its many derivatives have been test cases for the development of many computational methods and of force fields. The ability to get the structural, electronic and magnetic properties of this system correct is a very important benchmark for these efforts. Deficiencies found here can be expected to be found in other systems. Many of the current force fields and XC function-

als—as sophisticated as they are—are not of an accuracy where they can be used as black box programs, and this is often underappreciated. Thus, as computational and theoretical chemists continue to explore ever more complex systems, there remains significant value in rigorous examination of systems that are better able, owing to structural simplicity and small size, to interrogate the accuracy of a given methodology. Modeling and comparison to experiment for the present suite of spectroscopic attributes provides a robust assessment. Hence, in this work we look at the geometries, vibrational frequencies, and VA, VCD, Raman and ROA intensities as a combined set to evaluate XC functionals within DFT, and the wave function quantum mechanics (WFQM) methods we have used. This is an update and extension of work begun in the Stephens and Keiderling laboratories nearly 20 years ago [1, 3]. Other groups have recommended alternative properties to determine the optimal X and C functionals and even formalisms: coupled perturbed Kohn–Sham equations, linear response theory, finite field perturbation theory, (electric) current DFT, and time dependent DFT (TDDFT). This is clearly beyond the scope of this work, and here we focus on geometries and vibrational properties (frequencies and intensities) to benchmark density functional [29] and wave function based semi-empirical methods [30, 31]. In addition, to benchmark electronic excited state methods, one requires not only accurate transition energies, but also oscillator strengths. The problems with the currently used TDDFT and DFT methods are still notable and much work needs to be undertaken before these methods can be used with uniform accuracy and reliability [32–55].

1.1 Synthesis of (+)-*trans*-1(S),2(S)-dicyanocyclopropane- d_0 and 1,2- d_2

The resolution of (+)-*trans*-1(S),2(S)-DCCP- d_0 , and 1,2- d_2 was performed on the dicarboxylic acid precursor. Brucine was used for the resolution according to the method of Shone et al. [56, 57]. The resolved *trans*-1,2-cyclopropane dicarboxylic acid d_0 and 1,2- d_2 had an optical rotation $[\alpha]_D = +208^\circ$ ($c = 1.19$, EtOH) and $+206^\circ$ ($c = 0.06$, EtOH) for CN2- d_0 and CN2-1,2- d_2 respectively, as compared to $+230$ ($c = 1.19$, EtOH) for CN2- d_0 reported by Heintz et al. [5], which implies a $\geq 90\%$ enantiomeric excess. The dicarboxylic acid was then used for the synthesis of the (+)-dicyano derivative as was described in Chap. 4 of El-Azhary's PhD thesis [3].

1.2 Theoretical methodology

With the Molden program, the structures of CP, cyanocyclopropane (CCP) and *trans*-, *cis*- and *gem*-DCCP were built and subsequently optimized with various exchange correlation

(XC) functionals (B3LYP/DZP level of theory with the Cambridge Analytical Derivatives Package (CADPAC) [58]). Preliminary work on these molecules has been presented at the Molecular Spectroscopy Conference in Columbus Ohio [59,60], in a JACS article [2], and in two PhD theses, one at the University of Southern California, Los Angeles, CA, USA [1]) and one at the University of Illinois-Chicago, Chicago, IL, USA [3]). The earlier research focused on the use of so-called scaled quantum mechanical (SQM) restricted Hartree–Fock (RHF) force fields [2,4]. This methodology has not only been used in vibrational analysis [61], but has also been the level of theory used to produce the second generation of molecular mechanics force fields still being used and modified in the commonly available programs and program packages, Gromos (Gromacs) [62], Charmm [63], NAMD [64], OPLS [65–67] and Amber [68–70]. The methodology is still very similar, but what has changed is the so-called zeroth order guess [71]. One can use RHF, which was used for many years, and subsequently one can go to MP2 or DFT with its many derivatives; LDA, the many GGAs, the many hybrids, the many meta-hybrids and the more recent XC functionals based on optimized effective potentials (OEPs) [72–74]. In this work we have utilized the DFT methods available in CADPAC in combination with the Dunning double-zeta basis set with polarization functions (DZP) [75]. In addition, for the highest accuracy we have utilized the aug-cc-pVTZ basis set and the B3PW91 hybrid XC functional, as this combination has been shown to give the best agreement with the complete set of vibrational spectra (VA, VCD, Raman and ROA) for phenyloxirane [22].

In this work we have utilized the main XC correlation functionals in the latest version of the Cambridge Analytical Derivatives Package (CADPAC). All of the functionals, except the BP86 and B3P86, allow one to simulate the VCD spectra. For these two functionals the geometry has been optimized and the Hessian and atomic polar tensors (APT) have been calculated by finite difference methods. The atomic axial tensors (AAT) have been calculated with the same basis set, but with the B3LYP hybrid exchange correlation functional. Here we wish to document the accuracy of the BP86 GGA and B3P86 hybrid XC functionals for use in modeling cyano compounds. Previously we have shown that the use of only a comparison of experimental and theoretical vibrational frequencies is not a good measure of the accuracy of a molecular force field [59,60,76]. Two force fields can have equivalent root mean square (RMS) differences for frequencies, but have very different RMS differences for the vibrational intensities [76]. Hence, it is also important to compare the experimental and theoretical VA intensities, as the VA intensities measure the accuracy of the APT and atomic displacements of the atoms for each normal mode. (Another experiment which can be used

to evaluate the accuracy of both the vibrational frequencies (eigenvalues) and the atomic displacements (eigenvectors) of the Hessian is inelastic neutron scattering (INS) [77].) The B3LYP/DZP level of theory is known to reproduce structures and energies to an accuracy approaching that achieved in good experimental work. But besides this, for comparison and testing other models, coordinate optimization by conjugate gradients and computing force constant matrices (Hessian matrices) for phonon calculations of *trans*-DCCP were performed using a self consistent density functional method implemented in the SIESTA code [78,79]. Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) is both a method and a computer program implementation, and uses standard norm-conserving pseudo-potentials and a flexible, numerical linear combination of atomic orbitals basis set. Exchange-correlation was treated with the generalized-gradient optimization as parametrized by Perdew-Burke-Ernzerhof (PBE) [80]. In our calculations we used a double-zeta single polarized basis set and an energy shift of 0.01 Rydbergs. We have used a cubic box with length 24 Å. For the geometry optimizations we have used a maximum force tolerance of 0.01 eV/Å and maximum conjugate gradient displacement of 0.05 Å. Our mesh cutoff was 250.0 Rydbergs. For our finite difference Hessians we have used three point difference of the analytic forces. Our displacement distance was 0.04 Bohr (1.0 Bohr = 0.529177 Å).

Finally we have used Gaussian 03 to optimize the geometry and calculate the VA, VCD, Raman and ROA spectra with the B3PW91 hybrid exchange correlation functional and the aug-cc-pVTZ basis set.

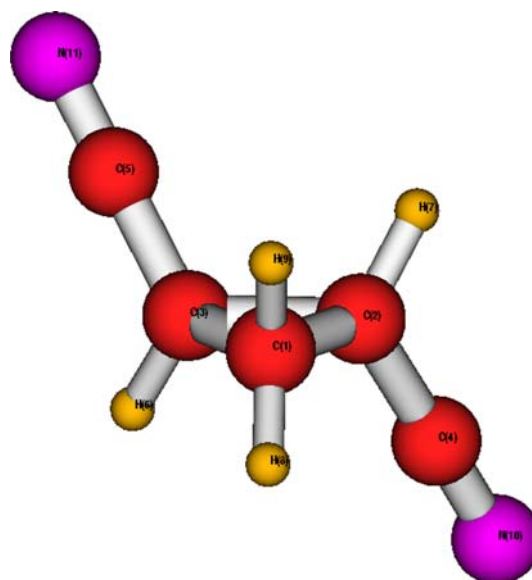


Fig. 1 *trans*-1(R),2(R)-DCCP

2 Results and discussion

2.1 Energetics of *trans*-1,2-DCCP

In Fig. 1 we present the structure of *trans*-1(R),2(R)-DCCP. In Table 1 we present the absolute energies for the non symmetrical *trans*-DCCP. With the hybrid XC PBE0 functional the absolute energies for the non symmetrical and symmet-

rical (C_2) structures were very similar. The geometries and frequencies were essentially the same. For molecules with symmetry, many programs use symmetry in the calculations, which can reduce the computational time. The disadvantage is that even if the molecule does not have symmetry in its lowest state, the molecule will ‘normally’ maintain the symmetry in the geometry optimization. Hence, it is very important to calculate the Hessian and diagonalize it, to see if all of

Table 1 *trans*-1,2-DCCP: total energies (Hartrees) for different methods/DFT (XC functionals) with the DZP and TZ/2P basis sets with CADPAC and for the B3PW91 hybrid XC functional with the aug-cc-pVTZ basis set with Gaussian 03

Method/DFT (XC-functional)	DZP	TZ/2P	aug-cc-pVTZ
RHF	−300.57172806	−300.62342841	
MP2	−301.62434965	−301.88353917	
BD	−301.65632601		
LDAX	−296.63267076	−296.71636283	
LDA	−299.75404773	−299.83970409	
BLYP	−302.30612290	−302.39377446	
B3LYP	−302.23308048	−302.31017658	
PBE0	−302.05884618	−302.12208509	
PBE	−302.04178666	−302.11465825	
B3P91	−302.29212713	−302.35909274	
BP91	−302.38088152	−302.45371956	
B3P86	−302.33170367	−302.39948001	
BP86	−302.42678351	−302.50085664	
HCTH	−302.31023574	−302.37147893	
HCTH147	−302.37896963	−302.44262477	
HCTH407	−302.36670032	−302.42866264	
B97	−302.28873950	−302.35833737	
B97-1	−302.32442588	−302.39253080	
B3PW91			−302.357779925

Table 2 *trans*-1,2-DCCP: geometrical parameters with various basis sets and BD

Geometry	STO-3G	3-21G	DZ	6-31G*	DZP
R(C ₁ C ₂)	1.5454	1.5365	1.5523	1.5060	1.5138
R(C ₂ C ₃)	1.5585	1.5503	1.5638	1.5218	1.5248
R(C ₂ C ₄)	1.4966	1.4480	1.4705	1.4491	1.4565
R(C ₄ N ₁₀)	1.2061	1.1717	1.1924	1.1651	1.1701
R(C ₁ H ₈)	1.1064	1.0859	1.0947	1.0858	1.0824
R(C ₂ H ₇)	1.1095	1.0865	1.0954	1.0870	1.0832
θ (C ₂ C ₁ C ₃)	60.56	60.60	61.49	60.69	60.48
θ (C ₁ C ₂ C ₄)	119.79	118.50	119.59	119.26	118.82
θ (C ₃ C ₂ C ₄)	118.83	117.55	118.47	117.81	117.57
θ (C ₂ C ₄ N ₁₀)	179.55	179.72	179.55	179.19	178.94
θ (C ₂ C ₁ H ₈)	117.60	117.19	117.44	117.44	117.24
θ (H ₈ C ₁ H ₉)	115.12	116.10	115.52	115.45	116.02
θ (C ₁ C ₂ H ₇)	117.03	117.45	117.13	117.65	117.87
θ (C ₃ C ₂ H ₇)	116.62	116.41	116.48	116.62	116.98

the eigenvalues are positive, which, if so, confirms that the structure is indeed a local minimum. But the question of the structure being the global minimum for the set of bond connectivities is still open to debate and investigation. This type of multiple minimum problem normally can be addressed by classical mechanics force fields and semi-empirical methods since the various conformers/isomers are due to rotation about single and double bonds. Here it depends on the barriers, but since the connectivities do not change, this type of isomerization is not a problem. But for bond isomerization, molecular mechanics force fields which use harmonic potentials for bonds (which require as input bond connectivities) there is no possibility for hydrogen transfer. A more physical bond potential is the Morse potential, used in vibrational spectroscopy. This potential also has the advantage of being able to treat both vibrational anharmonicity and also bond dissociation.

Recently we have shown that many of the currently used molecular mechanics force fields have a built in (due to parameterization) local minimum, which though stable for proteins, are not stable for small peptides in either the gaseous (isolated) state or in an aqueous environment [12, 14, 81, 82]. The advantage of first principles and ab initio WFQM and DFT based methods, is that by running Born–Oppenheimer molecular dynamics (BOMD) and non-BOMD (NBOMD) simulations under the conditions of the experiment (room temperature, solvent, counterions, electromagnetic radiation, either continuous or finite pulsed) one can actually observe the evolution of the system (chemical and physical evolution in time of real processes) albeit for a limited amount of real time. As computers get more powerful and methods more efficient, the length of computer simulations gets longer and longer, which has allowed some workers to make the choice to go to larger and more complex systems, but for others to keep the size of the system the same, but to model events which only occur at longer times. Finally so-called smart sampling techniques have been developed, with the goal to speed up the time it takes for improbable events to occur, for example, torsion forcing. Many of these methods initially were developed to find the global minimum and researchers were not really interested in more than structural information. More recently, researchers have tried to either use the current methods, extend them, or even develop new ones to be able to model chemical reactions and biological reactions and function [83–85]. This has been a very challenging problem, especially biological and chemical reactions which are photon initiated. Here one must not only deal with ground electronic state BOMD, but also electronic excited state BOMD and NBOMD simulations. How the initial excited state photon is absorbed and then either transferred to another chromophore in the molecule [fluorescence resonance energy transfer (FRET)] or ‘lost’ due to radiationless collisional transfer

is a very important and exciting problem. But this is beyond the scope of this work.

As one can see in Table 1, all of the correlated methods have absolute energies lower than the RHF values, except the LDA and LDAX methods. To evaluate the accuracy of a variational correlated method, one can look at the absolute energy. But for DFT methods the situation is not as straightforward. This is due to the nature of the approximations used for the XC functional and the use of a single Slater determinant to represent the electron density. The variational principle tells us that the HF wave function, and hence HF energy, is the best one can do using a single Slater determinant to represent the electronic wave function. But this only applies to the full and correct electronic Hamiltonian. Within Kohn–Sham theory, the assumption is that we can approximate the true exchange–correlation energy (and hence potential) using only a single Slater determinant of Kohn–Sham orbitals. The question of using these Kohn–Sham orbitals to then evaluate expectation values of other properties is a highly debated issue. To evaluate properties, one can utilize finite field perturbation theory, coupled perturbed Kohn–Sham theory or linear response theory. If one had the exact XC functional, the properties calculated within these formalisms would all agree, similar to the various formalisms for calculating the APT and AAT within HF theory at the HF limit [86–89]. Works by Rohra and Görling, Becke, Lee and Handy, and Malkin and Salahub, and Vignale and Rasolt have shown that many of the currently used XC functionals have not been parameterized adequately with respect to many of the perturbations of interest to molecular spectroscopists, time and frequency dependent electric fields, electric field gradients, and magnetic fields [48, 90–105].

2.2 Comparison of geometrical parameters and vibrational frequencies for *trans*-1,2-DCCP

In Table 2 we present the geometrical parameters for the optimized structure calculated at the Brueckner doubles (BD) level of theory with the STO-3G [106], 3-21G [107], DZ [75], 6-31G* [108] and DZP [75] basis sets. As one can see, there are significant changes when one goes from the minimal basis set (STO-3G) to the split valence (3-21G) and double-zeta (DZ) basis sets. Also, there is a noticeable difference between the split valence plus polarization functions on only C and N and the double zeta plus polarization functions on all atoms (C, N and H). Hence, for our comparison utilizing DFT, we use the DZP (Table 3 for geometry, Table 4 for vibrational frequencies) and TZ2P (Table 5 for geometry, Table 6 for vibrational frequencies) basis sets. In Table 7, we present the RMS differences for the various levels of theory with the experimental frequencies. With the DZP basis set, RHF theory is significantly less accurate. There is

Table 3 *trans*-1,2-DCCP: geometrical parameters for various methods/DFT (XC functionals) with the DZP basis set

Geometry	RHF	MP2	LDAX	LDA	B3LYP	BLYP	PBE0	PBE	B3P91	BP91	B3P86	BP86	HCTH	HCTH147	HCTH407	B97	B97-1
R(C ₁ C ₂)	1.5010	1.5132	1.5299	1.5081	1.5185	1.5328	1.5090	1.5228	1.5124	1.5241	1.5129	1.5250	1.5153	1.5150	1.5086	1.5249	1.5250
R(C ₂ C ₃)	1.5130	1.5278	1.5529	1.5301	1.5389	1.5549	1.5274	1.5464	1.5322	1.5487	1.5327	1.5494	1.5384	1.5379	1.5298	1.5468	1.5467
R(C ₂ C ₄)	1.4549	1.4462	1.4504	1.4313	1.4478	1.4527	1.4424	1.4462	1.4438	1.4475	1.4438	1.4476	1.4443	1.4436	1.4407	1.4499	1.4502
R(C ₄ N ₁₀)	1.1373	1.1872	1.1867	1.1741	1.1679	1.1808	1.1641	1.1800	1.1660	1.1793	1.1665	1.1800	1.1745	1.1746	1.1734	1.1667	1.1682
R(C ₁ H ₈)	1.0737	1.0824	1.1114	1.0951	1.0851	1.0918	1.0846	1.0926	1.0847	1.0910	1.0856	1.0922	1.0867	1.0870	1.0861	1.0855	1.0861
R(C ₂ H ₇)	1.0736	1.0838	1.1141	1.0980	1.0868	1.0941	1.0864	1.0950	1.0865	1.0933	1.0874	1.0945	1.0889	1.0892	1.0884	1.0871	1.0877
θ (C ₂ C ₁ C ₃)	60.53	60.64	61.00	60.97	60.89	61.11	60.81	61.03	60.87	61.07	60.87	61.06	61.01	61.00	60.94	60.95	60.94
θ (C ₁ C ₂ C ₄)	118.89	118.80	118.86	118.79	119.26	119.60	119.03	119.35	119.23	119.57	119.13	119.41	119.96	119.73	119.83	119.09	119.07
θ (C ₃ C ₂ C ₄)	117.65	117.39	117.26	117.18	117.80	117.96	117.53	117.73	117.73	117.90	117.62	117.75	118.28	118.09	118.24	117.59	117.55
θ (C ₂ C ₄ N ₁₀)	179.54	178.49	178.99	178.97	179.30	179.26	179.32	179.24	179.42	179.41	179.35	179.31	179.55	179.37	179.34	179.28	179.25
θ (C ₂ C ₁ H ₈)	117.39	117.10	117.06	117.06	117.18	117.12	117.17	117.09	117.18	117.13	117.16	117.10	117.22	117.18	117.24	117.11	117.10
θ (H ₈ C ₁ H ₉)	115.63	116.31	116.27	116.28	116.00	116.08	116.07	116.17	116.02	116.06	116.06	116.15	115.86	115.97	115.85	116.15	116.17
θ (C ₁ C ₂ H ₇)	118.45	117.57	117.77	117.77	117.73	117.41	117.91	117.56	117.78	117.49	117.83	117.55	117.38	117.45	117.43	117.88	117.88
θ (C ₃ C ₂ H ₇)	117.56	116.51	116.26	116.28	116.57	116.14	116.75	116.25	116.64	116.25	116.65	116.25	116.27	116.27	116.27	116.66	116.65

Table 4 *trans*-1,2-DCCP: vibrational frequencies for various methods/DFT (XC functionals) with the DZP basis set

Symmetry	Expt	RHF	MP2	BD	LDAX	LDA	B3LYP	BLYP	PBE0	PBE	B3P91	BP91	B3P86	BP86	HCTH	HCTH147	HCTH407	B-97	B97-1
B	3,119	3,439	3,293	2,023	3,085	3,205	3,273	3,194	3,307	3,216	3,292	3,220	3,286	3,211	3,259	3,258	3,275	3,274	3,273
B	3,052	3,387	3,279	1,969	3,005	3,119	3,201	3,116	3,232	3,136	3,218	3,141	3,210	3,131	3,178	3,176	3,191	3,202	3,202
A	3,052	3,386	3,275	1,965	3,004	3,118	3,199	3,114	3,231	3,134	3,216	3,139	3,210	3,128	3,176	3,173	3,189	3,201	3,201
A	3,035	3,336	3,237	1,958	2,984	3,099	3,170	3,092	3,200	3,111	3,187	3,117	3,188	3,127	3,152	3,150	3,167	3,168	3,167
B	2,247	2,593	2,295	1,457	2,215	2,288	2,331	2,224	2,370	2,248	2,346	2,245	2,344	2,243	2,276	2,276	2,288	2,332	2,327
A	2,247	2,592	2,182	1,455	2,211	2,284	2,329	2,220	2,368	2,244	2,344	2,241	2,342	2,238	2,272	2,273	2,285	2,329	2,324
A	1,443	1,635	1,545	942	1,383	1,432	1,488	1,440	1,498	1,435	1,490	1,442	1,489	1,425	1,462	1,458	1,464	1,484	1,481
A	1,385	1,550	1,459	878	1,324	1,367	1,411	1,355	1,427	1,366	1,418	1,368	1,416	1,364	1,389	1,388	1,394	1,403	1,402
B	1,297	1,436	1,308	815	1,217	1,253	1,309	1,266	1,315	1,262	1,309	1,268	1,308	1,260	1,287	1,284	1,286	1,304	1,301
A	1,190	1,314	1,256	764	1,144	1,180	1,208	1,162	1,227	1,178	1,218	1,178	1,217	1,174	1,197	1,196	1,205	1,199	1,200
B	1,131	1,254	1,147	700	1,065	1,095	1,141	1,104	1,146	1,102	1,141	1,106	1,141	1,103	1,119	1,117	1,118	1,138	1,136
B	1,104	1,217	1,132	697	1,035	1,064	1,105	1,069	1,112	1,069	1,107	1,073	1,104	1,070	1,087	1,085	1,088	1,104	1,102
A	1,075	1,216	1,112	670	993	1,023	1,083	1,043	1,087	1,036	1,082	1,042	1,087	1,041	1,056	1,053	1,051	1,083	1,079
A	1,048	1,186	1,110	641	988	1,020	1,070	1,030	1,077	1,028	1,072	1,033	1,064	1,028	1,048	1,046	1,049	1,067	1,065
B	992	1,090	974	639	983	1,018	1,017	979	1,044	1,004	1,033	1,001	1,029	999	1,018	1,018	1,032	1,004	1,005
B	908	1,041	923	575	869	899	933	894	943	898	937	900	942	898	916	914	919	925	924
A	871	1,005	903	557	847	890	883	827	925	864	907	857	905	850	881	881	907	855	859
A	809	884	822	505	774	802	816	781	829	793	823	793	845	789	805	805	808	812	812
B	778	852	599	494	761	789	790	759	808	777	800	774	802	775	786	787	795	778	779
B	553	614	512	345	529	545	555	532	564	539	559	538	560	539	549	549	553	551	551
B	530	586	504	326	499	514	525	503	533	508	528	507	527	506	519	518	524	521	520
A	518	576	476	320	492	507	516	494	524	500	518	498	518	497	508	509	512	512	511
A	497	544	413	306	471	486	490	467	501	476	494	474	491	471	484	486	489	486	486
B	270	289	229	134	238	244	255	244	257	244	255	244	256	244	249	252	246	250	249
A	327	251	211	134	208	213	224	214	224	213	223	214	224	212	220	223	216	220	219
B	129	167	102	92	139	142	151	146	150	144	149	143	150	143	145	148	139	142	142
A	88	127	-984	73	106	115	110	113	108	112	107	113	108	105	110	97	106	106	105

Table 5 *trans*-1,2-DCCP: geometrical parameters with various methods/DFT (XC functionals) with the TZ/2P basis set

Geometry	RHF	MP2	LDAX	LDA	B3LYP	BLYP	PBE0	PBE	B3P91	BP91	B3P86	BP86	HCTH	HCTH147	HCTH407	B97	B97-1
R(C ₁ C ₂)	1.4961	1.5036	1.5192	1.4966	1.5082	1.5211	1.5008	1.5132	1.5033	1.5143	1.5037	1.5149	1.5069	1.5063	1.5008	1.5139	1.5144
R(C ₂ C ₃)	1.5098	1.5221	1.5451	1.5216	1.5315	1.5506	1.5218	1.5397	1.5259	1.5417	1.5262	1.5424	1.5328	1.5318	1.5247	1.5385	1.5388
R(C ₂ C ₄)	1.4477	1.4345	1.4401	1.4207	1.4374	1.4416	1.4335	1.4364	1.4343	1.4373	1.4342	1.4373	1.4352	1.4342	1.4318	1.4398	1.4403
R(C ₄ N ₁₀)	1.1265	1.1684	1.1696	1.1569	1.1509	1.1633	1.1501	1.1643	1.1512	1.1634	1.1516	1.1638	1.1599	1.1595	1.1584	1.1519	1.1537
R(C ₁ H ₈)	1.0706	1.0763	1.1068	1.0902	1.0790	1.0847	1.0802	1.0874	1.0799	1.0857	1.0806	1.0867	1.0823	1.0822	1.0812	1.0804	1.0810
R(C ₂ H ₇)	1.0706	1.0772	1.1096	1.0932	1.0806	1.0867	1.0820	1.0897	1.0818	1.0880	1.0824	1.0890	1.0845	1.0843	1.0834	1.0821	1.0826
θ (C ₂ C ₁ C ₃)	60.61	60.81	61.13	61.11	61.03	61.29	60.93	61.16	61.00	61.20	60.99	61.21	61.14	61.12	61.06	61.08	61.07
θ (C ₁ C ₂ C ₄)	119.19	118.77	119.39	119.38	119.79	120.16	119.43	119.81	119.66	120.01	119.57	119.88	120.38	120.18	120.31	119.52	119.50
θ (C ₃ C ₂ C ₄)	117.86	117.25	117.67	117.63	118.16	118.37	117.84	118.02	118.01	118.18	117.92	118.07	118.57	118.38	118.55	117.89	117.85
θ (C ₂ C ₄ N ₁₀)	179.42	178.39	179.04	179.04	179.34	179.39	179.26	179.26	179.36	179.45	179.30	179.35	179.56	179.41	179.40	179.24	179.22
θ (C ₂ C ₁ H ₈)	117.37	116.98	117.06	117.08	117.22	117.17	117.14	117.10	117.18	117.14	117.17	117.11	117.24	117.20	117.25	117.15	117.13
θ (H ₈ C ₁ H ₉)	115.66	116.53	116.22	116.17	115.85	115.88	116.09	116.10	115.97	116.00	115.99	116.06	115.78	115.88	115.77	116.01	116.07
θ (C ₁ C ₂ H ₇)	118.13	117.49	117.46	117.44	117.40	117.11	117.60	117.28	117.48	117.21	117.52	117.27	117.11	117.17	117.11	117.58	117.58
θ (C ₃ C ₂ H ₇)	117.26	116.26	115.89	115.89	116.24	115.82	116.39	115.92	116.30	115.92	116.31	115.93	115.95	115.95	115.95	116.34	116.33

Table 6 *trans*-1,2-DCCP: vibrational frequencies for various methods/DFT (XC functionals) with the TZ/2P basis set

Symmetry	Expt	RHF	MP2	LDAX	LDA	B3LYP	BLYP	PBE0	PBE	B3P91	BP91	B3P86	BP86	HCTH	HCTH147	HCTH407	B-97	B97-1
B	3,119	3,397	2,370	3,056	3,175	3,247	3,173	3,273	3,186	3,261	3,192	3,251	3,177	3,227	3,227	3,243	3,244	3,243
B	3,052	3,347	2,321	2,978	3,092	3,178	3,101	3,203	3,110	3,189	3,116	3,201	3,122	3,148	3,148	3,164	3,176	3,176
A	3,052	3,346	2,305	2,975	3,089	3,175	3,097	3,200	3,107	3,186	3,113	3,193	3,118	3,144	3,144	3,159	3,173	3,173
A	3,035	3,302	2,286	2,962	3,076	3,153	3,081	3,174	3,090	3,163	3,096	3,147	3,072	3,127	3,127	3,143	3,146	3,146
B	2,247	2,590	1,567	2,230	2,305	2,347	2,244	2,377	2,260	2,357	2,269	2,355	2,274	2,284	2,286	2,296	2,345	2,338
A	2,247	2,589	1,564	2,227	2,301	2,344	2,240	2,375	2,256	2,355	2,256	2,355	2,256	2,280	2,282	2,292	2,343	2,336
A	1,443	1,627	1,072	1,376	1,424	1,492	1,450	1,491	1,434	1,487	1,442	1,480	1,436	1,457	1,457	1,459	1,486	1,482
A	1,385	1,544	1,009	1,326	1,370	1,417	1,366	1,426	1,368	1,419	1,370	1,414	1,371	1,388	1,387	1,394	1,409	1,406
B	1,297	1,440	945	1,232	1,269	1,330	1,292	1,324	1,278	1,323	1,285	1,330	1,286	1,300	1,298	1,298	1,320	1,316
A	1,190	1,302	862	1,147	1,187	1,208	1,164	1,225	1,179	1,217	1,178	1,213	1,176	1,195	1,194	1,204	1,202	1,202
B	1,131	1,255	832	1,073	1,104	1,153	1,119	1,151	1,110	1,149	1,115	1,154	1,115	1,125	1,124	1,126	1,147	1,144
B	1,104	1,218	820	1,044	1,074	1,117	1,084	1,118	1,078	1,115	1,083	1,117	1,078	1,094	1,093	1,096	1,114	1,111
A	1,075	1,218	802	1,008	1,039	1,102	1,065	1,096	1,051	1,095	1,058	1,092	1,050	1,067	1,067	1,065	1,096	1,091
A	1,048	1,184	794	998	1,028	1,081	1,044	1,082	1,037	1,079	1,042	1,087	1,042	1,055	1,054	1,057	1,075	1,073
B	992	1,072	727	983	1,022	1,013	978	1,038	1,001	1,028	998	1,018	986	1,013	1,012	1,026	1,004	1,005
B	908	1,034	691	872	902	938	903	941	900	937	903	940	907	917	916	922	928	926
A	871	982	641	839	881	870	821	910	853	893	847	898	851	868	868	891	851	854
A	809	878	603	775	805	819	781	828	794	823	794	833	785	805	805	810	813	812
B	778	841	586	759	788	788	759	803	774	797	772	821	778	782	783	791	777	778
B	553	613	407	537	553	562	542	569	546	566	547	566	548	556	557	563	557	557
B	530	587	387	506	520	533	513	538	515	535	516	541	507	525	526	533	527	526
A	518	575	384	498	513	523	504	528	506	526	508	538	503	515	516	522	518	517
A	497	544	348	476	492	495	473	504	481	500	481	498	479	488	490	496	490	490
B	270	290	205	245	251	258	246	257	244	258	246	265	251	257	255	260	259	256
A	327	251	187	213	217	224	214	222	211	223	214	249	219	226	223	228	225	223
B	129	168	145	143	145	147	139	143	135	146	138	167	142	153	146	159	153	149
A	88	128	97	109	111	108	100	105	96	107	98	124	112	114	105	120	117	114

Table 7 *trans*-1,2-DCCP: RMS differences from experimental vibrational frequencies

DZP	Percentage	TZ2P	Percentage
RHF	12.6	RHF	12.1
MP2	7.9	MP2	26.3
BD	37.7	BD	
LDAX	5.5	LDAX	5.2
LDA	4.0	LDA	3.4
B3LYP	4.0	B3LYP	4.0
BLYP	4.6	BLYP	3.6
PBE0	5.0	PBE0	4.8
PBE	4.0	PBE	3.3
B3P91	4.4	B3P91	4.3
BP91	3.9	BP91	3.2
B3P86	4.5	B3P86	4.8
BP86	4.2	BP86	3.4
HCTH	3.6	HCTH	3.2
HCTH147	3.6	HCTH147	3.0
HCTH407	3.7	HCTH407	3.6
B-97	3.7	B-97	3.9
B97-1	3.7	B97-1	3.7

a noticeable improvement with MP2 theory. With DFT theory, LDAX is better than RHF and MP2, but not as good as the generalized gradient approximation (GGA) XC functionals. The hybrid XC functionals are slightly better than the GGA functionals. In our previous works with scaled quantum mechanical (SQM) force fields we showed that the RMS difference from the calculated and experimental frequencies can be reduced significantly [1–4]. In most quantum mechanical programs, for example, a uniform scaling of the frequencies can be performed. Here one just shifts all of the frequencies and the relative order of the modes does not change. When one performs a more sophisticated scaling of the quantum mechanical force constants, one must answer four questions: first, how many scale factors do you want to use; second, what set of internal coordinates do you use, simple valence internal coordinates or local symmetry internal coordinates; third, how to group the internal coordinates with the scale factors; and finally what set of experimental data does one use in the scaling. In early works many researchers used simple valence internal coordinate [109–113], while later works used local symmetry internal coordinates [1, 2, 76].

When one observes that the order of modes one calculates with a given force field is not the same as that determined experimentally, one must during the scaling get the order of the two modes to flip. When one groups the same simple valence internal coordinates with one scale factor this is not possible. Hence it is very important to use local symmetry internal coordinates, and in addition, use separate scale fac-

tors for the two modes which are calculated to have the wrong relative ordering. We have done this for *trans*-1(R),2(R)-DCCP and have shown that one can correct RHF force fields calculated with the 6-31G** and 6-31Gext [58] basis sets with this methodology, which previously many thought could not be done, albeit by using only simple valence internal coordinates and only one scale factor.

Only with very sophisticated correlated methods can one achieve the accuracy which can be achieved with sophisticated SQM force fields which use local symmetry valence internal coordinates. The advantage, of course, of the sophisticated correlated methods is that they are thought to be general, systematic and also do not require any experimental data. The disadvantage is the additional cost. But with computing power becoming better and better and the recently developed ab initio DFT methods using optimized effective potentials, the scaling of lower level force fields against experimental data may become moot. Our RMS deviations from experiment with our RHF/6-31G** force fields were 182 cm⁻¹ (unscaled), 37 cm⁻¹ (uniform scaled, one scale factor) and 13 cm⁻¹ (six scale factors) [2, 1]. El-Azhary [4, 3] got similar results with both SQM force fields and with force fields where one refines force constants, rather than, scale factors. The SQM force fields well produced the VA and VCD spectra for both *trans*-1(R),2(R)-DCCP and *trans*-1(R),2(R)-DCCP-1,2-d₂ [1]. For complete details of the methodology, which is beyond the scope of this work, see the PhD theses of Jalkanen, USC, 1989 [1] and El-Azhary, UIC, 1990 [3]. With the advent of MP2 and DFT force fields, the need to perform sophisticated scaling of force fields has been diminished, since the MP2 and DFT force fields are of an accuracy which many consider good enough. If one requires very accurate force fields, one may wish to utilize the methods discussed in the theses of Jalkanen and El-Azhary to scale MP2, CC and DFT force fields.

But the use of the experimental data is still good in quality controlling the new ab initio and DFT based methods, in addition to the WFQM and DFT based semi-empirical methods and next generation of classical molecular mechanics force fields. If one wishes to perform BOMD and NBOMD simulations to get the vibrational spectra by Fourier transform methodology, then one should make sure the method is accurate enough to reproduce the vibrational spectra for similar compounds, molecules, or complexes under the same conditions: pH, ionic strength, temperature and pressure.

The BD level of theory actually does much worse than DFT methods, but this is due to the geometry being significantly different, with the CP ring opening. This is also seen at the MP2 level of theory with the TZ2P basis set [114]. With the TZ2P basis set the DFT results are improved versus those with the smaller DZP basis set, as expected. The Handy XC functionals appear to be better than the B3LYP hybrid XC functional, which has been the functional of choice for

Table 8 Experimental vibrational frequencies [6], relative IR/VA and Raman intensities and depolarization ratios [4] for *trans*-1(S),2(S)-DCCP and the B3PW91 hybrid XC functional with the aug-cc-pVTZ basis set for *trans*-1(R),2(R)-DCCP. $D_i \times 10^{-40}$ and $R_i \times 10^{-44}$

Symmetry	Expt[6] (cm^{-1})	Symmetry	IR [4] (cm^{-1})	Relative intensity	Ram (cm^{-1})	Relative intensity	Polar ratio	B3PW91 (cm^{-1})	Symmetry	IR/VA D_i	VCD R_i	Raman	Polar ratio
B	3,119	B	3,116	42	3,120	13	0.73	3,258	B	0.39	-0.40	49.1	0.75
B	3,052	B	3,056	123				3,188	B	3.67	-2.48	9.7	0.07
A	3,052	A			3,050	64	0.23	3,185	A	0.50	0.28	133.4	0.75
A	3,035	A	3,031	sh	3,031	54	0.00	3,161	A	0.59	-0.09	102.3	0.11
B	2,247	B	2,256	301				2,361	B	76.30	-7.69	36.2	0.51
A	2,247	A			2,243	102	0.15	2,359	A	6.93	0.06	376.8	0.75
A	1,443	A	1,446	18	1,448	57	0.38	1,482	A	9.03	-15.34	28.8	0.38
A	1,385	A	1,389	4	1,390	72	0.31	1,420	A	0.81	6.47	32.0	0.16
B	1,297	B	1,297	2	1,297	5	0.75	1,323	B	1.31	3.40	2.3	0.75
A	1,190	A	1,189	9	1,191	118	0.11	1,218	A	3.33	-12.41	24.3	0.07
B	1,131	B	1,129	8	1,130	6	0.91	1,147	B	1.33	7.92	2.6	0.75
B	1,104	A	1,095	sh	1,099	7	0.15	1,112	A	0.64	-2.47	1.0	0.75
A	1,075	B	1,074	78				1,088	B	18.02	19.10	1.5	0.74
A	1,048	A	1,052	121	1,059	8	0.80	1,077	A	29.89	7.07	5.1	0.75
B	992	B	991	100	994	14	0.78	1,032	B	66.95	43.32	6.3	0.70
B	908	B	912	42	912	28	0.72	935	B	24.23	-8.18	6.3	0.39
A	871	A	870	43	870	60	0.72	898	A	27.40	-5.38	23.4	0.75
A	809	A	805		805	61	0.30	822	A	1.98	-6.49	11.3	0.75
B	778	B	785		790	sh		798	B	39.77	-21.79	4.1	0.13
B	553	B	550	24				565	B	9.93	-9.78	0.2	0.75
B	530	B	521	2				538	B	4.12	-0.81	0.2	0.20
A	518	A	510		512	7		527	A	0.37	-0.78	0.9	0.76
A	497	A	491	30	490	13		503	A	11.96	21.71	4.1	0.12
B	270	B			265	sh	1.00	262	B	3.37	13.26	2.8	0.76
A	237	A	235		229	12	0.45	228	A	24.62	-34.86	3.3	0.51
B	129	B	143					154	B	420.05	-24.63	0.4	0.75
A	88	A						116	A	534.67	7.86	2.0	0.75

many quantum chemists. Recently the alternative, B3PW91 or B3P86 hybrid exchange correlation functionals have also been advocated, due to the lack of dispersion seen in the B3LYP XC functional. There has been a lot of recent work on developing XC functionals for dispersion forces, the best being the recent work by the Bartlett group using optimized effective potentials [73, 115, 116]. A discussion of the work on dispersion forces and hydrogen bonding is beyond the scope of this work. For a more complete discussion of these works, see the paper on L-alanine and *N*-acetyl L-alanine *N'*-methylamide in this issue [11].

In Table 8 we compare the experimental frequencies and symmetries from Schrupp and Dunker [6] and the frequencies, symmetries, IR/VA and Raman relative intensities and Raman polarization ratios of El-Azhary et al. [4] with our calculated vibrational frequencies, symmetries, IR/VA and Raman intensities and Raman depolarization ratios. Our simulations are in agreement with all of the symmetry orderings

of Schrupp and Dunker [6] except for the relative order of the experimental bands at $1,104\text{ cm}^{-1}$ (B) and $1,075\text{ cm}^{-1}$ (A). Our ordering is that the higher frequency mode at $1,113\text{ cm}^{-1}$ is of A symmetry (D_i of 0.64×10^{-40}) and the next mode at $1,088\text{ cm}^{-1}$ is of B symmetry (D_i of 18.02×10^{-40}). Our assignment of these two modes is consistent with the reassignment of Schrupp and Dunker's modes by El-Azhary et al. [4]. In Table 8 we bold type set the modes where there has been disagreement on the assignment of the symmetries. Hence for *trans*-1(R),2(R)-DCCP, our highest level calculation with the B3PW91 hybrid XC functional and the aug-cc-pVTZ basis set is consistent with the experimentally determined SQM force fields. Hence this level of theory appears to accurately reproduce the experimental VA, VCD and Raman spectra for *trans*-1(R),2(R)-DCCP.

A further test of the force field is to see if it also reproduces the experimental VA, VCD and Raman spectra for isotopomers of DCCP. Isotopomers have been used in the past during

Table 9 Experimental vibrational frequencies, relative IR/VA and Raman intensities and depolarization ratios [4] for *trans*-1(S), 2(S)-DCCP-1, 2-d₂ and B3PW91 hybrid XC functional with the aug-cc-pVTZ basis set for *trans*-1(R), 2(R)-DCCP-1, 2-d₂. D_i × 10⁻⁴⁰ and R_i × 10⁻⁴⁴

Symmetry	IR cm ⁻¹	Relative intensity	Ram cm ⁻¹	Relative intensity	Polar ratio	B3PW91 cm ⁻¹	Symmetry	IR/VA D _i	VCD R _i	Raman	Polar ratio
B	3,116	50	3,116	7	0.76	3,258	B	0.30	-1.10	51.3	0.75
A	3,032	2	3,031	37	0.12	3,161	A	0.65	-0.05	111.1	0.07
B			2,301	19	0.10	2,368	B	54.29	-2.30	27.8	0.75
A	2,270	171	2,271	7		2,367	A	2.72	-1.30	338.4	0.11
A	2,251	600				2,344	A	4.68	3.00	98.7	0.51
B			2,247	77	0.17	2,339	B	24.25	-7.94	12.0	0.75
A	1,444	45	1,443	38	0.51	1,477	A	9.27	-7.79	18.9	0.38
A	1,327	3	1,327	88	0.10	1,365	A	0.55	2.15	54.1	0.16
B	1,149	34	1,149	70	0.81	1,178	B	6.24	-13.29	5.5	0.75
A	1,113	7	1,112	53	0.08	1,135	A	1.92	-4.40	11.7	0.07
B	1,073	114				1,088	B	19.01	19.65	1.4	0.75
B	998	100	1,000	9	0.60	1,019	B	41.55	33.09	3.1	0.75
A	925		925	30	0.66	945	A	0.77	0.12	16.0	0.74
B	885	49	885	11	0.71	901	B	20.25	9.00	3.4	0.75
A	872					888	A	0.45	3.42	0.6	0.70
A	827	51	825	72	0.38	848	A	16.22	4.57	18.8	0.39
B	815	74				839	B	20.60	-12.91	6.6	0.75
B	732	105				746	B	34.17	-7.60	1.8	0.75
A	720	47				732	A	19.42	-14.36	4.6	0.13
B	545	43				560	B	10.16	-9.54	0.2	0.75
B	496	14				513	A	3.55	2.80	0.1	0.29
A			488	22	0.20	504	B	0.97	0.24	0.1	0.75
A	483	40				498	A	9.14	18.71	4.5	0.12
B			265	3		260	B	3.72	13.67	2.8	0.75
A	231		224	6		222	A	23.53	-33.40	3.2	0.51
B	143					147	B	432.72	-22.11	0.5	0.75
A						114	A	531.15	7.66	2.0	0.75

the refinement of the force constants, and later to determine the scale factors. Within the BO approximation, one can use the same force field to predict the harmonic frequencies for all isotopomers of a molecule. In Table 9 we compare the experimental frequencies, symmetries, IR/VA and Raman relative intensities and Raman polarization ratios of El-Azhary et al. [4] with our calculated vibrational frequencies, symmetries, IR/VA and Raman intensities and Raman depolarization ratios using the B3PW91 hybrid XC functional and the aug-cc-pVTZ basis set for *trans*-1(R), 2(R)-DCCP-1, 2-d₂. Here the B3PW91/aug-cc-pVTZ level calculation is in agreement with the assignments of El-Azhary et al. [3, 4] and Jalkanen [1] (Table 9).

In Fig. 2 we present the experimental VA and VCD spectra for (+)-*trans*-1(S), 2(S)-DCCP in the CH stretch region. In Fig. 3 we present the experimental VA and VCD spectra for *trans*-1(S), 2(S)-DCCP in the CN stretch region. In Fig. 4 we present the experimental VA and VCD spectra for (+)-*trans*-

1(S), 2(S)-DCCP-1(S), 2(S)-d₂ in the CN stretch region. In Fig. 5 we present the experimental VA and VCD spectra for (+)-*trans*-1(S), 2(S)-DCCP in the mid-IR. In Fig. 6 we present the experimental VA and VCD spectra for (+)-*trans*-1(S), 2(S)-DCCP-1(S), 2(S)-d₂ in the mid-IR region. In Fig. 7 we present the simulated VA and VCD spectra for *trans*-1(R), 2(R)-DCCP in the mid-IR region at the B3PW91/aug-cc-pVTZ level of theory. In Fig. 8 we present the simulated VA and VCD spectra for *trans*-1(R), 2(R)-DCCP-1(R), 2(R)-d₂ in the mid-IR region at the B3PW91/aug-cc-pVTZ level of theory. As one can see, at this highest level of theory one is able to well reproduce the VA and VCD spectra, as was done by Jalkanen et al. [1, 2] and El-Azhary et al. [3, 4] with SQM force fields, but with no need to scale the force fields with experimental data. Hence the ability to predict the VA and VCD spectra from first principles calculations. The only experimental fits have been the parameters in the B3PW91 hybrid XC functional. But in the fit the experimen-

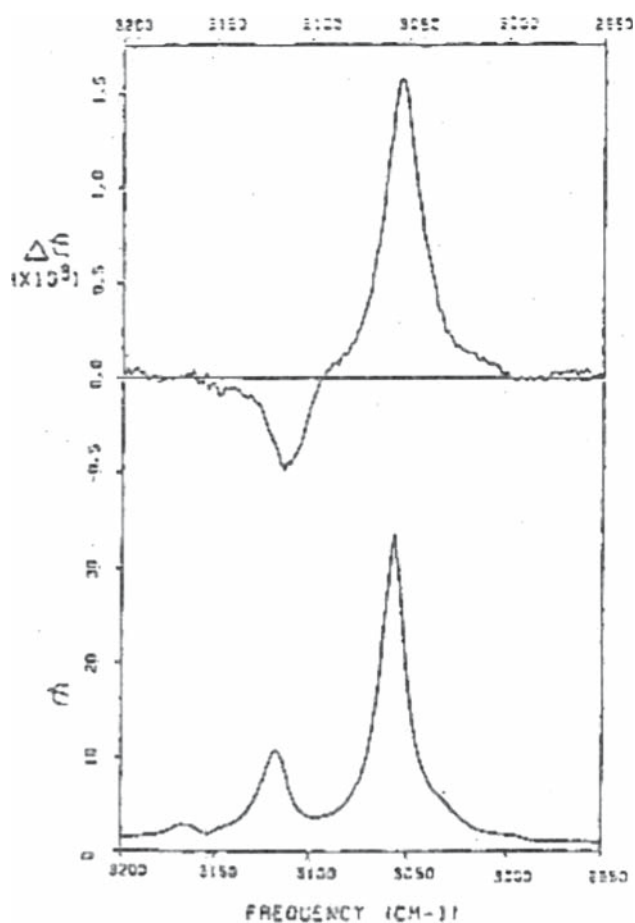


Fig. 2 VCD spectra and VA spectra of (+)-*trans*-1(S),2(S)-DCCP- d_0 in the C–H stretch region: 0.110 M in $CDCl_3$, path length = 0.15 cm, four scan average with time constant = 10 [3]

tal vibrational frequencies and VA and VCD intensities was not used. By being able to reproduce accurately the VA and VCD spectra, the parameterization appears to be general. What would be even better is the use of a so-called *ab initio* DFT XC functional, as those being developed and tested by the Bartlett group, the so-called optimized effective potentials [73, 115, 116]. But to be able to utilize this level of theory, the analytical Hessians, electric field and magnetic field perturbations, both static and frequency dependent, need to be implemented. This is a work in progress, but it is clearly one way to proceed for the prediction of VA and VCD spectra of biomolecules.

Finally in Figs. 9 and 10 we present the experimental Raman spectra for *trans*-1,2-DCCP and *trans*-1,2-DCCP-1,2- d_2 and in Figs. 11 and 12 the corresponding the Raman (and ROA) theoretical simulations, again at the B3PW91 hybrid XC functional and the aug-cc-pVTZ basis set. The Raman spectra is well reproduced, again documenting the reliability of this level of theory, not only for VA and VCD spectral simulations, but also for Raman spectral simulations.

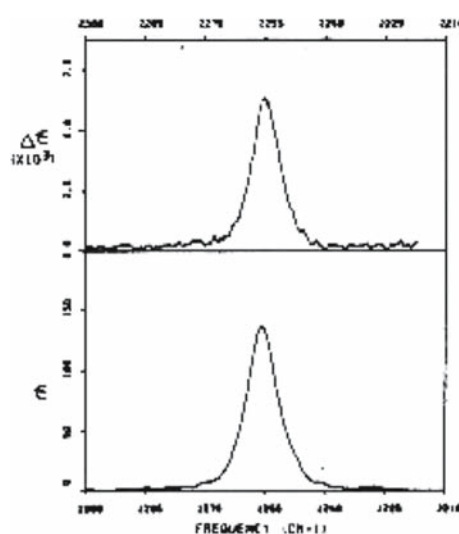


Fig. 3 VCD spectra and VA spectra of (+)-*trans*-1(S),2(S)-DCCP- d_0 in the C–N stretch region: 0.044 M in $CDCl_3$, path length = 0.10 cm, three scan average with time constant = 10 [3]

We present the ROA spectral simulations for both *trans*-1(R),2(R)-DCCP and *trans*-1(R),2(R)-DCCP-1(R),2(R)- d_2 . This data can be used as a further check on the ability of this level of theory to reproduce the ROA spectra for this molecule, which has been quite a challenge at the RHF level of theory, and required one to scale the RHF level force fields to get not only good agreement with the frequencies, but also the VA, VCD, and Raman intensities. Very little work has been presented on SQM force fields for ROA. Most of the ROA simulations have been compared directly to the experimental ROA spectra. But with the recent implementation of ROA in CADPAC, Dalton and now Gaussian 03, the theoretical prediction of ROA spectra in nonpolar and non strongly interacting solvent has become straightforward and routine. The prediction of the VA, VCD, Raman and ROA spectra of molecules in polar and strongly interacting solvents and environments is currently a very challenging problem. Some of the more recent works have been undertaken by groups which have also presented works in this special issue. See the paper by Deplazes et al., for example, on L-histidine in this special issue [16] and the paper by Jalkanen et al. on L-alanine and *N*-acetyl L-alanine *N'*-methylamide [11].

2.3 Comparison of geometrical parameters for CP, CCP, *gem*-1,1-DCCP, *cis*-1,2-DCCP and *trans*-1,2-DCCP

In Table 10 we present the geometrical parameters of for CP and its monocyno- and dicycano-substituted derivatives at the B3PW91/aug-cc-pVTZ level of theory. As one can see the C–C bond length varies from 1.4994 Å in CP to 1.5125 Å (lengthening) and 1.4894 Å (shortening) for CCP, 1.5287 Å (lengthening) and 1.4796 (shortening) for *gem*-1,

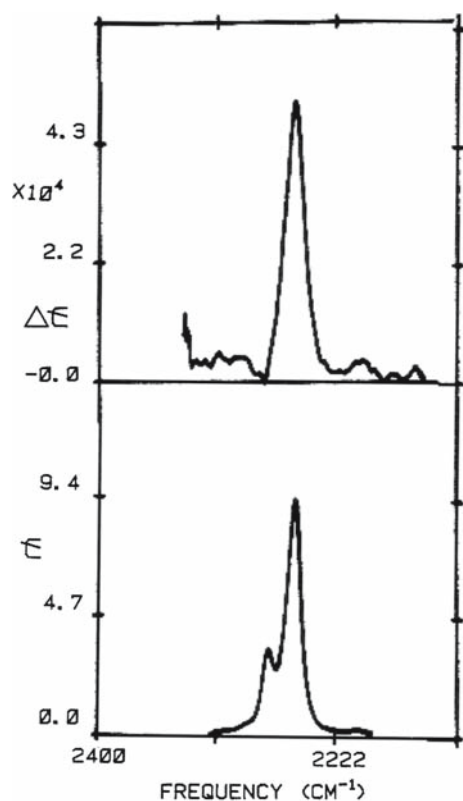


Fig. 4 VCD spectra and VA spectra of (+)-*trans*-1(S),2(S)-DCCP-1(S),2(S)- d_2 in the C–N stretch region [3]

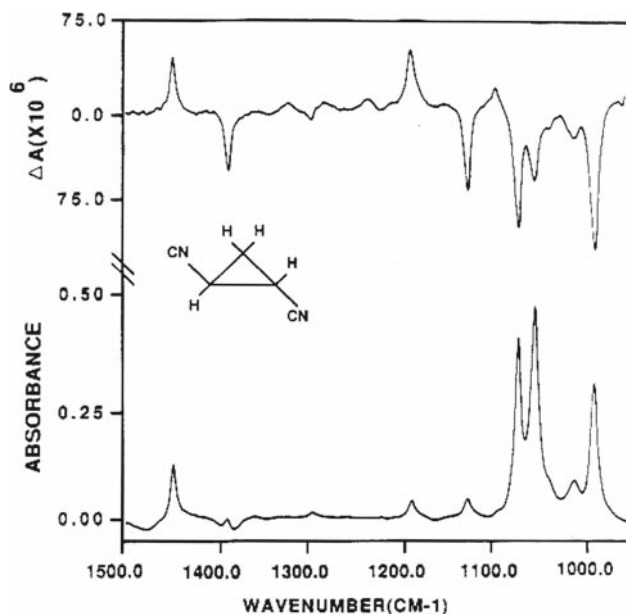


Fig. 5 VCD spectra and VA spectra of (+)-*trans*-1(S),2(S)-DCCP- d_0 in the mid-ir region: 0.476 M in $CDCl_3$, path length = 0.023 cm, 8,192 scan average with 4 cm^{-1} resolution [3]

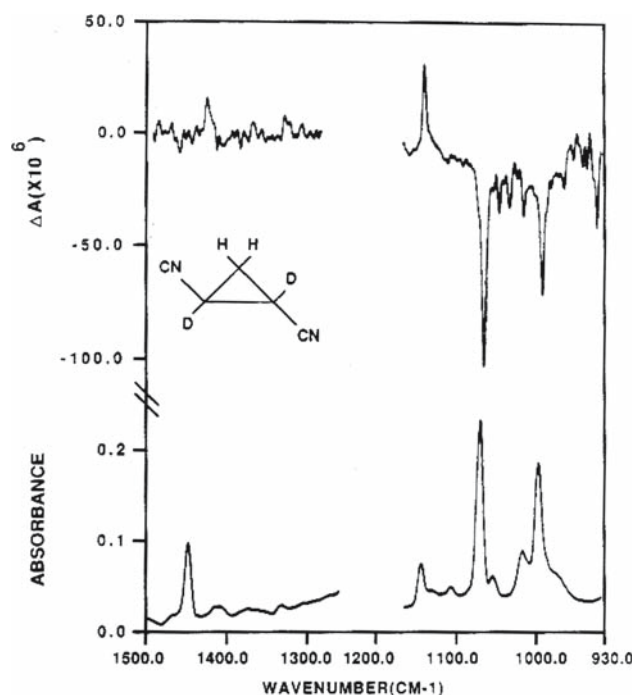


Fig. 6 VCD spectra and VA spectra of (+)-*trans*-1(S),2(S)-DCCP-1(S),2(S)- d_2 in the mid-ir region: 0.567 M in $CDCl_3$, path length = 0.020 cm, 16,384 scan average with 4 cm^{-1} resolution [3]

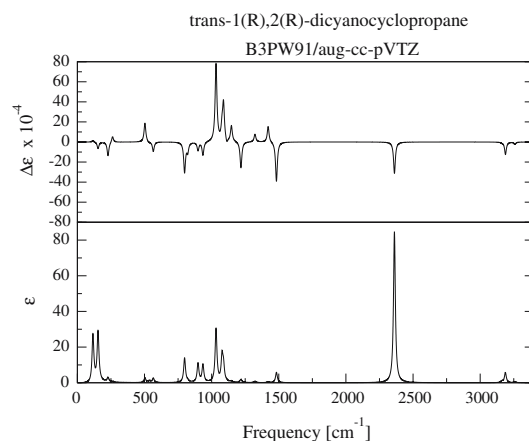


Fig. 7 Theoretical VA and VCD spectra *trans*-1(R),2(R)-DCCP, B3PW91/aug-cc-pVTZ level of theory

1-DCCP, 1.5253 Å (lengthening) and 1.5024 Å (lengthening) for *cis*-1,2-DCCP and 1.5246 Å (lengthening) and 1.5023 Å (lengthening) for *trans*-1,2-DCCP. For CCP and *gem*-1, 1-DCCP, the C–C[–C(N)] bonds are lengthened and the C–C bond is shortened, and the ring thus has a conjugated multiple bond character. Surprisingly, in both *cis*-1,2- and *trans*-1,2-DCCP, the C–C[–C(N)] bonds are lengthened with respect to the C–C bond in CP, as is the [(N)C]–C–C[–C(N)] bond, but to a lesser degree. The C–H bond length varies from 1.0818 Å in CP to 1.0807 Å (shortening) [cis to CN], 1.0811 Å (shortening) [trans to CN] and 1.0823 Å (lengthening) [gem to CN] for CCP. The hydrogen bond length that is length-

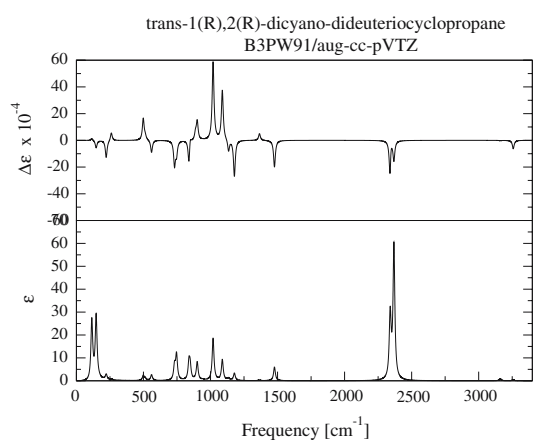


Fig. 8 Theoretical VA and VCD spectra *trans*-1(R),2(R)-DCCP-1(R),2(R)-d₂, B3PW91/aug-cc-pVTZ level of theory

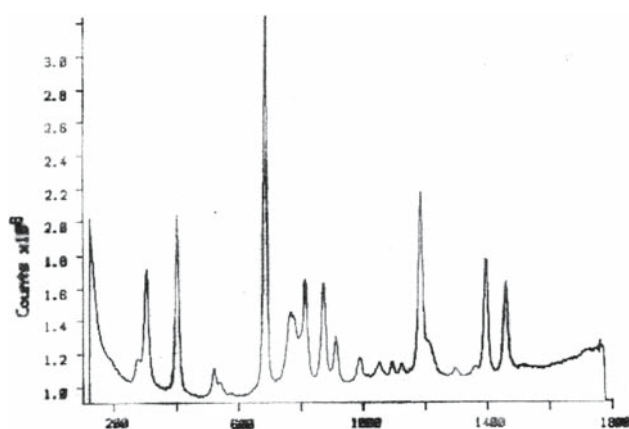


Fig. 9 Raman spectrum of *trans*-1,2-DCCP-d₀ in CHCl₃, calibrated by indene for the 1,500–1,700 cm⁻¹ region [3]

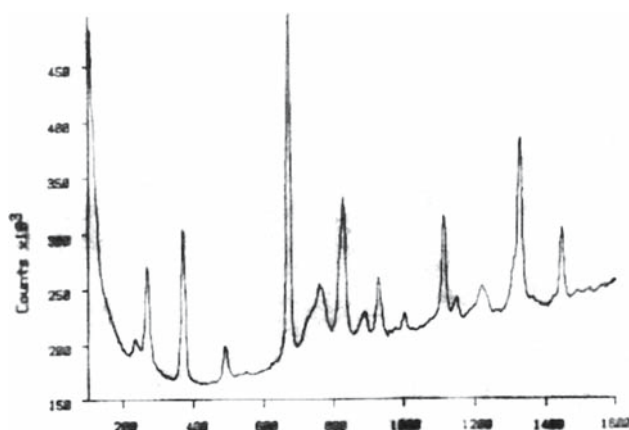


Fig. 10 Raman spectrum of *trans*-1,2-DCCP-1,2-d₂ in CHCl₃, calibrated by indene for the 1,500–1,700 cm⁻¹ region [3]

ened is the one which is attached to the carbon bonded to the CN group [labelled gem]. For the DCCP derivatives, the C–H bond lengths are 1.0806 Å for the four CH₂ (methine) CH bond lengths for gem, 1.0806 Å and 1.0802 Å for the two CH₂ (methylene) CH bond lengths and 1.0826 Å for the

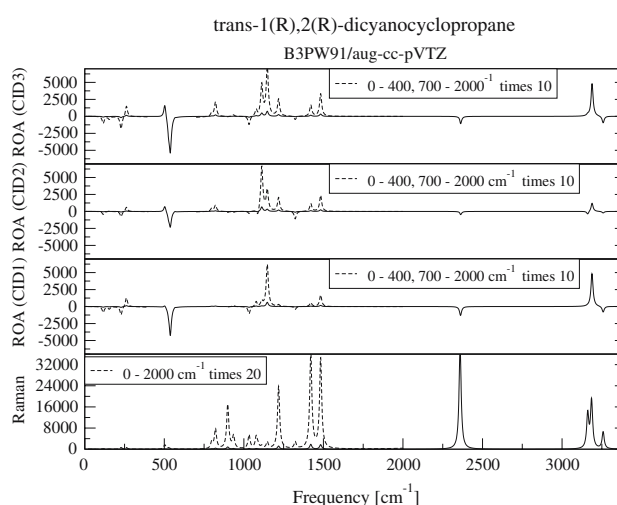


Fig. 11 Theoretical Raman and ROA (CID1, CID2, CID3) spectra *trans*-1(R),2(R)-DCCP, B3PW91/aug-cc-pVTZ level of theory

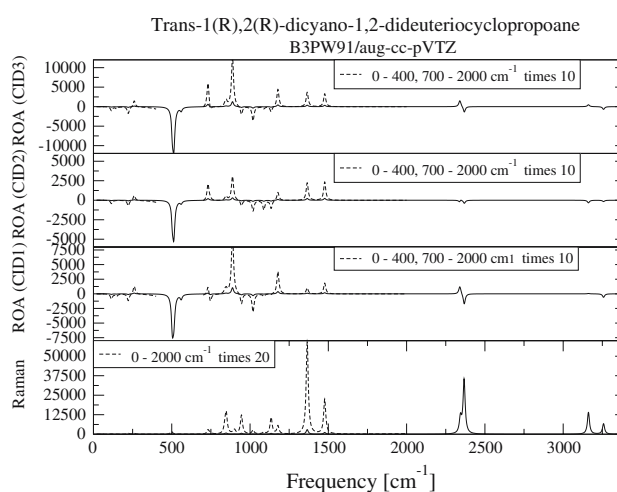


Fig. 12 Theoretical Raman and ROA (CID1, CID2, CID3) spectra *trans*-1(R),2(R)-DCCP-1(R),2(R)-d₂, B3PW91/aug-cc-pVTZ level of theory

two CH (methine) CH bond lengths for cis, and 1.0802 Å for the two CH₂ (methylene) ring CHs and 1.0821 Å for the CH (methine) ring CHs for trans. The C–N bond length varies from 1.1522 Å in CCP, to 1.1508 Å for *gem*-1,1-DCCP, 1.1509 Å for *cis*-1,2-DCCP and 1.1515 Å for *trans*-1,2-DCCP. The C–C(N) bond length varies from 1.4315 Å in CCP to 1.4381 Å for *gem*-1,1-DCCP, 1.4321 Å for *cis*-1,2-DCCP and 1.4324 Å for *trans*-1,2-DCCP.

2.4 Changes in the VA, VCD and Raman spectra of *trans*-1,2-DCCP

Now we shall look for spectroscopic markers for changes due to only using different XC functionals. This is sometimes neglected when comparing theoretical results to experiment;

Table 10 Geometrical parameters for CP, CCP, *gem*-DCCP, *cis*-DCCP and *trans*-DCCP, B3PW91/aug-cc-pVTZ

Geometry	CP	Geometry	CCP	Geometry	<i>gem</i> -DCCP	Geometry	<i>cis</i> -DCCP	Geometry	<i>trans</i> -DCCP
R(C ₁ C ₂)	1.4994	R(C ₁ C ₂)	1.5125	R(C ₁ C ₂)	1.5287	R(C ₁ C ₂)	1.5253	R(C ₁ C ₂)	1.5262
R(C ₁ C ₃)	1.4994	R(C ₁ C ₃)	1.5125	R(C ₁ C ₃)	1.5287	R(C ₁ C ₃)	1.5024	R(C ₁ C ₃)	1.5037
R(C ₂ C ₃)	1.4994	R(C ₂ C ₃)	1.4894	R(C ₂ C ₃)	1.4796	R(C ₂ C ₃)	1.5024	R(C ₂ C ₃)	1.5037
R(C ₁ H ₄)	1.0818	R(C ₁ H ₄)	1.0823	R(C ₁ H ₄)	1.0823	R(C ₁ H ₄)	1.0826	R(C ₁ H ₄)	1.0824
				R(C ₁ C ₄)	1.4381				
R(C ₁ H ₅)	1.0818	R(C ₁ C ₅)	1.4315	R(C ₁ C ₅)	1.4381	R(C ₁ C ₅)	1.4321	R(C ₁ C ₅)	1.4342
R(C ₂ H ₆)	1.0818	R(C ₂ H ₆)	1.0811	R(C ₂ H ₆)	1.0806	R(C ₂ H ₆)	1.0826		
								R(C ₂ C ₆)	1.4342
R(C ₂ H ₇)	1.0818	R(C ₂ H ₇)	1.0807	R(C ₂ H ₇)	1.0806			R(C ₂ H ₇)	1.0824
						R(C ₂ C ₇)	1.4321		
R(C ₃ H ₈)	1.0818	R(C ₃ H ₈)	1.0811	R(C ₃ H ₈)	1.0806	R(C ₃ H ₈)	1.0806	R(C ₃ H ₈)	1.0806
R(C ₃ H ₉)	1.0818	R(C ₃ H ₉)	1.0807	R(C ₃ H ₉)	1.0806	R(C ₃ H ₉)	1.0802	R(C ₃ H ₉)	1.0806
				R(C ₄ N ₁₁)	1.1508				
		R(C ₅ N ₁₀)	1.1522	R(C ₅ N ₁₀)	1.1508	R(C ₅ N ₁₀)	1.1509	R(C ₅ N ₁₀)	1.1516
								R(C ₆ N ₁₁)	1.1516
						R(C ₇ N ₁₁)	1.1509		
θ (C ₂ C ₁ C ₃)	60.00	θ (C ₂ C ₁ C ₃)	58.99	θ (C ₂ C ₁ C ₃)	57.89	θ (C ₂ C ₁ C ₃)	59.495	θ (C ₂ C ₁ C ₃)	59.503
θ (C ₁ C ₂ C ₃)	60.00	θ (C ₁ C ₂ C ₃)	60.50	θ (C ₁ C ₂ C ₃)	61.06	θ (C ₁ C ₂ C ₃)	59.495	θ (C ₁ C ₂ C ₃)	59.503
θ (C ₁ C ₃ C ₂)	60.00	θ (C ₁ C ₃ C ₂)	60.50	θ (C ₁ C ₃ C ₂)	61.06	θ (C ₁ C ₃ C ₂)	61.010	θ (C ₁ C ₃ C ₂)	60.993
				θ (C ₁ C ₄ C ₁₁)	178.19				
		θ (C ₁ C ₅ N ₁₀)	179.67	θ (C ₁ C ₅ N ₁₀)	178.19	θ (C ₁ C ₅ N ₁₀)	178.83	θ (C ₁ C ₅ N ₁₀)	179.30
								θ (C ₂ C ₆ N ₁₁)	179.30
						θ (C ₂ C ₇ N ₁₁)	178.83		
θ (C ₂ C ₁ H ₄)	118.07	θ (C ₂ C ₁ H ₄)	117.20			θ (C ₂ C ₁ H ₄)	114.81	θ (C ₂ C ₁ H ₄)	116.31
				θ (C ₂ C ₁ C ₄)	117.67				
θ (C ₂ C ₁ H ₅)	118.07								
		θ (C ₂ C ₁ C ₅)	119.35	θ (C ₂ C ₁ C ₅)	117.67	θ (C ₂ C ₁ C ₅)	120.75		
θ (C ₃ C ₁ H ₄)	118.07	θ (C ₃ C ₁ H ₄)	117.20						
				θ (C ₃ C ₁ C ₄)	117.67	θ (C ₃ C ₁ H ₄)	117.31	θ (3C ₁ H ₄)	117.52
θ (C ₃ C ₁ H ₅)	118.07								
		θ (C ₃ C ₁ C ₅)	119.35	θ (C ₃ C ₁ C ₅)	117.67	θ (C ₃ C ₁ C ₅)	120.10	θ (C ₃ C ₁ C ₅)	119.57
θ (H ₄ C ₁ H ₅)	114.19								
		θ (H ₄ C ₁ C ₅)	114.06			θ (H ₄ C ₁ C ₅)	113.91	θ (H ₄ C ₁ C ₅)	114.88
				θ (C ₄ C ₁ C ₅)	115.90				
θ (C ₁ C ₂ H ₆)	118.07	θ (C ₁ C ₂ H ₆)	116.39	θ (C ₁ C ₂ H ₆)	115.46	θ (C ₁ C ₂ H ₆)	114.81		
								θ (C ₁ C ₂ C ₆)	117.92
θ (C ₁ C ₂ H ₇)	118.07	θ (C ₁ C ₂ H ₇)	116.99	θ (C ₁ C ₂ H ₇)	115.46			θ (C ₁ C ₂ H ₇)	116.31
						θ (C ₁ C ₂ C ₇)	120.75		
θ (C ₃ C ₂ H ₆)	118.07	θ (C ₃ C ₂ H ₆)	118.77	θ (C ₃ C ₂ H ₆)	118.83	θ (C ₃ C ₂ H ₆)	117.31		
								θ (C ₃ C ₂ C ₆)	119.57
θ (C ₃ C ₂ H ₇)	118.07	θ (C ₃ C ₂ H ₇)	118.16	θ (C ₃ C ₂ H ₇)	118.83			θ (C ₃ C ₂ H ₇)	117.52
						θ (C ₃ C ₂ C ₇)	120.10		
θ (H ₆ C ₂ H ₇)	114.19	θ (H ₆ C ₂ H ₇)	115.10	θ (C ₆ C ₂ H ₇)	115.73			θ (C ₆ C ₂ H ₇)	114.88
						θ (H ₆ C ₂ C ₇)	113.91		
θ (C ₁ C ₃ H ₈)	118.07	θ (C ₁ C ₃ H ₈)	116.39	θ (H ₁ C ₃ H ₈)	115.46	θ (H ₁ C ₃ H ₈)	117.44	θ (H ₁ C ₃ H ₈)	115.99
θ (C ₁ C ₃ H ₉)	118.07	θ (C ₁ C ₃ H ₉)	116.99	θ (H ₁ C ₃ H ₉)	115.46	θ (H ₁ C ₃ H ₉)	117.07	θ (H ₁ C ₃ H ₉)	115.99
θ (C ₂ C ₃ H ₈)	118.07	θ (C ₂ C ₃ H ₈)	118.77	θ (H ₂ C ₃ H ₈)	118.83	θ (H ₂ C ₃ H ₈)	117.44	θ (H ₂ C ₃ H ₈)	115.99
θ (C ₂ C ₃ H ₉)	118.07	θ (C ₂ C ₃ H ₉)	118.16	θ (H ₂ C ₃ H ₉)	118.83	θ (H ₂ C ₃ H ₉)	117.07	θ (H ₂ C ₃ H ₉)	115.99
θ (H ₈ C ₃ H ₉)	114.19	θ (H ₈ C ₃ H ₉)	115.10	θ (H ₈ C ₃ H ₉)	115.73	θ (H ₈ C ₃ H ₉)	115.79	θ (H ₈ C ₃ H ₉)	115.99

that is, what is the magnitude of the difference by utilizing different theoretical methods. In many cases, the results are not only quantitatively different, but qualitatively so. Here we have started from the *trans*-1,2-DCCP structure (with an intact 3-membered ring) and found with certain XC functionals, that the ring opened. This is a surprising result, and is due to the underestimation of the ring opening barrier, i.e., the barrier is actually zero; a gross and qualitative difference! This results in a totally different, and fictional, topology for the potential energy surface. Hence, one must be very careful in drawing conclusions based on an XC functional for a system where analogous systems have not been adequately tested. To date, the B3LYP hybrid appears to be the best for molecules that do not have a stable minimum, which are only due to dispersion forces, e.g., as noted in DNA base stacking. For many chemical systems, there are two commonly used methods for adding electron correlation to the HF method, Møller–Plesset perturbation theory to second order (MP2) or density functional theory. In many cases, MP2 appears to be slightly better, but for the case of *trans*-1,2-DCCP, MP2 as commonly implemented, does worse. This has also been recognized by other researchers, and consequently MP2 has been extended to treat these systems in a variety of alternative ways: MRMP2 (multi-reference MP2) being one of the commonly used methods. Other alternatives include BD, and CC (coupled clusters) methods. We have performed both along with various DFT methods. For the case of TDCCP, the DFT methods appear to be better than simple MP2 or BD and competitive with CC methods, but at a cheaper cost [117, 118]. Hence for CP derivatives DFT methods utilizing hybrid XC functionals appear to be the best compromise between accuracy and computational cost. Since they are not yet fully ab initio methods, they need to be tested for each new chemical system. A good benchmark can be inferred from adequately high quality experimental results and CC methods. Assuming this is true, we conclude that the B3PW91 hybrid XC functional with the aug-cc-pVTZ basis set provides almost quantitative results, in agreement with our previous results for phenyloxirane [22]. In addition to being able to reproduce the VA, VCD, Raman and ROA vibrational spectra, it has recently been shown that a good test of a molecular force field is its ability to reproduce the INS spectra [77, 119–124]. Here one only needs the vibrational eigenvalues and eigenvectors and not the APT, AAT, electric dipole–electric dipole polarizability derivatives (EDEDPD), electric dipole–electric quadrupole polarizability derivatives (EDEQPD) and electric dipole–magnetic dipole polarizability derivatives (EDMDPD) which are required to simulate VA, VCD, Raman and ROA intensities. In addition, the low frequency modes are accessible via INS spectra, which in many cases are not available via IR or Raman, either due to low intensities or instrumental cutoffs. Hence, in the future it would be preferable to simulate the INS spectra, in

addition to the VA, VCD, Raman and ROA spectra, as the ability of theoretical force fields to reproduce the INS spectra is a further test for the method. The INS spectra is especially important for periodic systems, where the theory for VCD and ROA is yet to be developed.

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