improved understanding of photobleaching and -degradation of aromatic hydrocarbons under ambient conditions. More generally, the study of chemical reactions at the level of single molecules promises novel insights into mechanisms, product distributions, and the reaction kinetics.[1]

Experimental Section

Thin crystalline platelets of *p*-terphenyl doped with terrylene were prepared by cosublimation. In a typical single-molecule experiment first an image ($10 \times 10\ \mu m^2$) was taken with an inverted confocal microscope by raster scanning the sample through the objective focus (numerical aperture: 0.9). Then single molecules were positioned in the focus and fluorescence time traces and spectra were recorded. By using a two-channel detection scheme, the fluorescence light was simultaneously detected by an avalanche photodiode (time traces) and imaged through a spectrograph onto a liquid N_2 cooled CCD (spectra). The microscope allowed the purging of the sample with oxygen, air, or argon.

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Parity Violation Dominates the Dynamics of Chirality in Dichlorodisulfane**

Robert Berger, Michael Gottselig, Martin Quack,* and Martin Willeke

Nearly seventy five years ago, Friedrich Hund contemplated chirality by introducing the quantum mechanical tunnel effect.[1] He explained the origin of molecular chirality as de facto symmetry breaking[2] in relation to the small magnitude of the tunneling splitting $\Delta E_{\pm}$ between the delocalized lowest energy levels of well defined parity (+ and −), an explanation which held prior to the discovery of parity violation in 1956.[3, 4] Now, with electroweak quantum chemistry[5–7] taking the parity-violating nature of the weak interaction into account, we expect a small parity-violating energy difference ΔE_{pv} (about $10^{-13\pm3}\ J\,mol^{-1}$ for molecules consisting of lighter elements) between two enantiomers of a chiral molecule.[5–12] The discovery[6, 7, 10] that ΔE_{pv} is larger by an order of magnitude than previously anticipated has given new impetus to the search for molecular parity violation. Our early results[6, 7] have meanwhile been confirmed by further theoretical calculations.[10–12] For typical, stable chiral molecules with a high energetic barrier against interconversion between enantiomers, $|\Delta E_{pv}|$ should be as a rule much larger than the small tunneling splittings $|\Delta E_{\pm}|$ in the lowest vibrational states. In this case the molecular eigenfunctions have well defined handedness and molecular chirality arises from de lege symmetry breaking. Although this most striking situation is qualitatively predicted,[2, 5] there exists so far no such case for which a quantitative calculation has shown that $\Delta E_{pv} \gg \Delta E_{\pm}$ holds and thus chirality is dominated by de lege parity violation. Here, we present the first such example: dichlorodisulfane (ClSSCl, Figure 1).

Dichlorodisulfane has a chiral C_2-symmetric equilibrium structure with high barriers against interconversion between the *P*- and *M*-enantiomer (Figure 2) and has been previously investigated experimentally and by traditional (parity conserving) quantum chemical calculations on the general series X_2S_2.[13–18] We report here calculations of parity-violating potentials, the corresponding parity-violating energy differences, and the torsional tunneling splitting in the vibrational ground state for ClSSCl, which demonstrate that indeed parity violation dominates the dynamics of chirality in this molecule. Our theoretical findings on dichlorodisulfane and related compounds might prove crucial for experimental

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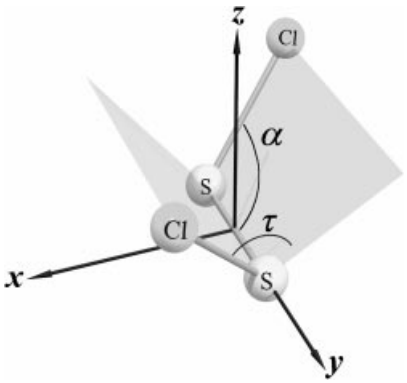

Figure 1. Chiral, C_2-symmetric equilibrium structure and orientation of the *P*-enantiomer of ClSSCl (corresponding to the left minimum in Figure 2) as used in the calculations presented here. It was obtained by a full structure optimization using second-order Møller–Plesset perturbation theory (MP2) in the frozen-core limit with a 6-311 + G(3df) basis set. Our results are consistent with experimental data as well as recent ab initio results.[13, 14, 18] The equilibrium structural parameters are r_e(S–S) = 194.7 pm, r_e(S–Cl) = 205.2 pm, $\alpha = 107.55°$, $\tau = 85.12°$.

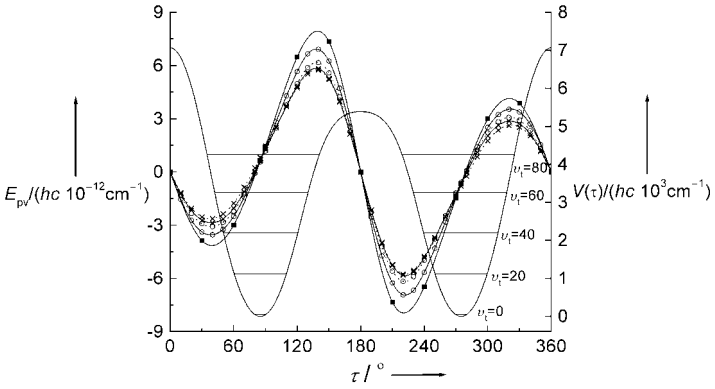

Figure 2. Parity-conserving electronic torsional potential $V(\tau)$ and parity-violating potentials $E_{pv}(\tau)$. $V(\tau)$ (solid line, right axis) was calculated in 10° steps along the torsional coordinate τ employing MP2/6-311 + G(3df). Values of τ between 0° and 180° correspond to the *P*-enantiomer while values of τ between 180° and 360° correspond to the *M*-enantiomer of ClSSCl. $V(\tau = 180°)$ corresponds to the *trans* barrier and $V(\tau = 0°)$ to the *cis* barrier to stereomutation, respectively. $E_{pv}(\tau)$ for different basis sets were calculated along the torsional coordinate in 10° steps (30° for cc-pVTZ-A) and additionally for the equilibrium torsional angle of ClSSCl using MP2/6-311 + G(3df) optimized structures. With an effective one-electron spin–orbit coupling operator,[10] and $Z_{eff}(S) = 12.9$, $Z_{eff}(Cl) = 13.9$ we were able to use a completely decontracted cc-pVTZ basis set additionally augmented with four s- and four p-Gaussian basis functions. The s- and p-like functions added to the sulfur atoms have orbital exponents of $\alpha_{s1}(S) = 2\,497\,000$, $\alpha_{s2}(S) = 16\,670\,000$, $\alpha_{s3}(S) = 111\,200\,000$, $\alpha_{s4}(S) = 742\,400\,000$, $\alpha_{p1}(S) = 2430$, $\alpha_{p2}(S) = 10\,280$, $\alpha_{p3}(S) = 43\,470$, and $\alpha_{p4}(S) = 183\,900$, while those added to chlorine atoms have orbital exponents of $\alpha_{s1}(Cl) = 3\,044\,000$, $\alpha_{s2}(Cl) = 20\,320\,000$, $\alpha_{s3}(Cl) = 135\,600\,000$, $\alpha_{s4}(Cl) = 905\,400\,000$, $\alpha_{p1}(Cl) = 2806$, $\alpha_{p2}(Cl) = 11\,870$, $\alpha_{p3}(Cl) = 50\,210$, and $\alpha_{p4}(Cl) = 212\,400$ (we denote this basis set "cc-pVTZ-A"). The assignment of symbols is as follows: squares and solid line (E_{pv}(RPA/cc – pVTZ – A)); circles and dashed line (E_{pv}(RPA/aug – cc – pVDZ)); crosses and dashed line (E_{pv}(RPA/cc – pVDZ)); circles and solid line (E_{pv}(RPA/6 – 311G(d))); crosses and solid line (E_{pv}(RPA/6 – 31G(d))). Some torsional levels ν_t are indicated.

efforts to directly measure ΔE_{pv} as well as to experimentally discriminate between different theories concerning the physicochemical origin of molecular chirality.[2, 19]

In the present calculations of the parity-violating potentials and the parity-violating energy difference between the *M*- and *P*-enantiomers of ClSSCl, we used our recent multiconfiguration linear response (MC-LR) approach[10] to electroweak quantum chemistry in the limits of the random phase approximation (RPA). Figure 2 shows the results. An important aspect in the present calculations concerns the determination of the very small hypothetical tunneling splittings $\Delta E_{\pm}$ for the parity-conserving, symmetrical potential. The direct variational calculation of the extremely small torsional tunneling splitting in the lowest vibrational states by means, for instance, of the quasiadiabatic channel–reaction path Hamiltonian approach (RPH)[21–23] is not possible due to numerical limitations. Therefore, we use an extrapolation technique to determine the tunneling splitting $\Delta E_{\pm}$. First, we calculated, with the RPH approach, the torsional tunneling splittings $\Delta E_{\pm}(f)$ for various scaled torsional potentials $V(\tau;f) = fV(\tau)$, where τ is the torsional coordinate, f is the scaling factor, and $V(\tau)$ is the unscaled, symmetrical, and thus parity-conserving effective torsional potential with the Born–Oppenheimer electronic potential and the zero-point corrections as the main contributions. The scaling factors were chosen so as to allow accurate numerical computations of the torsional splittings $\Delta E_{\pm}(f)$. Second, we fit the torsional splittings $\Delta E_{\pm}(f)$ with the simple relationship of Equation (1), where P_1, P_2, and P_3 are fit parameters.

$$\lg\left(\frac{\Delta E_{\pm}(f)}{hc\,\mathrm{cm}^{-1}}\right) = P_1 \lg\sqrt{f} + P_2 - P_3\sqrt{f} \qquad (1)$$

Then, we used these parameters and Equation (1) to extrapolate the torsional tunneling splittings $\Delta E_{\pm}(f)$ to $f = 1$. The ground-state torsional tunneling splitting for the original, unscaled torsional potential is thus given by Equation (2).

$$\Delta E_{\pm} = \Delta E_{\pm}(f=1) = (hc)10^{P_2 - P_3}\,\mathrm{cm}^{-1} \qquad (2)$$

Figure 3 displays the calculated torsional tunneling splittings $\Delta E_{\pm}$ as well as the excellent fit with Equation (1). With

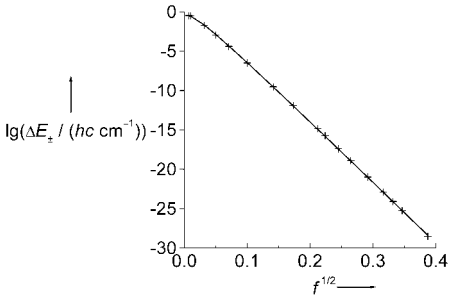

Figure 3. Decadic logarithm of the torsional tunneling splittings $\Delta E_{\pm}(f)$ for differently scaled torsional potentials $V(\tau,f) = fV(\tau)$ calculated with the quasiadiabatic channel–reaction path Hamiltonian approach (+ for RPH) and fit to Equation (1) (line).

the fit parameters $P_1 = 1.16(5)$, $P_2 = 2.59(10)$, and $P_3 = 78.73(24)$, and Equation (1), we obtained $\Delta E_{\pm}/hy \approx 10^{-76}\,\mathrm{cm}^{-1}$ for the ground-state tunneling splitting of ClSSCl. The physical significance of our fit formula can be discussed in terms of a recently presented expression for the ground-state tunneling splitting in a symmetric double-well potential $V(x)$

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obtained by the semiclassical Wentzel–Kramers–Brillouin (WKB) theory,[24] Equation (3).

$$\Delta E_{\pm} = 2\hbar\omega\sqrt{\frac{m\omega a^2}{\pi\hbar}}\mathrm{e}^{A}\mathrm{e}^{-S_0/\hbar} \tag{3}$$

The terms S_0 and A are given in Equations (4) and (5), respectively, where ω is the classical angular oscillation frequency of the small amplitude motion around the quadratic wells at $x = a$ and $x = -a$, and m is the reduced mass.

$$S_0 = \int_{-a}^{a}\sqrt{2\,m\,V(x)}\,\mathrm{d}x \tag{4}$$

$$A = \int_{0}^{a}\left[\frac{m\omega}{\sqrt{2\,m\,V(x)}} - \frac{1}{a-x}\right]\mathrm{d}x \tag{5}$$

Scaling of the symmetric double-well potential $V(x;f) = fV(x)$ results in a scaled classical angular harmonic oscillation frequency $\omega(f) = \sqrt{f}\,\omega(f=1)$. Insertion of $V(x;f)$ and $\omega(f)$ into the WKB formula (3) yields the ground-state tunneling splitting as a function of the scaling factor f, which can be written in the form of our fit formula (1) with $P_1 = 3/2$, $P_2 = \lg(2\hbar\omega\sqrt{m\omega a^2/\pi\hbar})\,\mathrm{e}^{A}/J$), and $P_3 = S_0/(\hbar\ln 10)$. In this case of a double-well potential, only one barrier at $x = 0$ is assumed to be finite and contributing to the tunneling dynamics. However, the torsional potential of ClSSCl has two paths with relatively similar barriers that contribute to the torsional tunneling splitting in a six-dimensional tunneling dynamic.[22, 23] Nevertheless, taking P_1, P_2, and P_3 as pure fit parameters we are able to fit the torsional tunneling splittings calculated by RPH for the two-barrier problem. Thus, WKB theory supports our extrapolation scheme. Moreover, we were able to establish good fit results in test calculations for hydrogen peroxide H_2O_2 and various disulfanes X_2S_2 (X = H, D, T) for which accurate experimental and theoretical results are available.[22, 23] In all cases we observe a nearly linear dependence between $\lg(\Delta E_{\pm}(f)/(hc\ \mathrm{cm}^{-1}))$ and $\sqrt{f}$ for large scaling factors. Since $\sqrt{f}$ is proportional to the number of torsional states N, which fit in the harmonic approximation into the well, $\lg(\Delta E_{\pm}(f)/(hc\ cm^{-1}))$ is also proportional to N. The terms $E_{\mathrm{pv}}(\tau)$ and $\Delta E_{\mathrm{pv}} = E_{\mathrm{pv}}(P\text{-enantiomer}) - E_{\mathrm{pv}}(M\text{-enantiomer})$ were obtained using the MC-LR approach to electroweak quantum chemistry in the limit of the random phase approximation.[10] Figure 2 displays $E_{\mathrm{pv}}(\tau)$ calculated with our modified[10] version of the Dalton program[20] for different basis sets. $E_{\mathrm{pv}}(\tau)$ shows the typical dependence on τ with large excursions from negative values for the P-enantiomer (that is, (P)-ClSSCl is stabilized compared to the M-form for $0^\circ < \tau < 80^\circ$), $E_{\mathrm{pv}}(\tau \approx 80^\circ) = 0$ at a chiral geometry,[7] to positive values for the P-enantiomer (namely, (M)-ClSSCl is stabilized), as was also found for H_2O_2 and H_2S_2.[7, 10, 25] Table 1 summarizes ΔE_{pv} for the equilibrium structure of ClSSCl. The values show that (M)-ClSSCl is stabilized compared to (P)-ClSSCl by about $10^{-12}\,\mathrm{cm}^{-1}$. Furthermore, the calculation of the two lowest torsional levels ($\Delta E^{\mathrm{pv}}_{0,1}$) with $E_{\mathrm{pv}}(\tau)$ added to the original effective torsional potential leads to $\Delta E^{\mathrm{pv}}_{0,1}/hc = 1.35 \times 10^{-12}\,\mathrm{cm}^{-1}$ (cc-pVTZ-A, see Figure 2) which is almost equal to $\Delta E_{\mathrm{pv}}/hc = 1.29 \times 10^{-12}\,\mathrm{cm}^{-1}$ for the equilibrium geometry and equal to the expectation values $\langle\Delta E_{\mathrm{pv}}\rangle$ for the localized vibrational states.

Table 1. Parity-violating energy difference $\Delta E_{\mathrm{pv}} = E_{\mathrm{pv}}(P) - E_{\mathrm{pv}}(M)$ for the optimized equilibrium structure of ClSSCl (Figure 1) calculated with different basis sets and MC-LR/RPA.

Method/Basis Set	$\Delta E_{\mathrm{pv}}/hc\ [10^{-12}\,\mathrm{cm}^{-1}]$
RPA/6-31G(d)	1.31
RPA/6-311G(d)	1.29
RPA/cc-pVDZ	1.62
RPA/aug-cc-pVDZ	1.14
RPA/cc-pVTZ-A	1.29

An increase in basis set size lowers the parity-violating energy difference slightly, but it still remains about 64 orders of magnitude larger than the torsional tunneling splitting in the lowest vibrational states, Equation (6).

$$|\Delta E_{\mathrm{pv}}|/hc \approx 10^{-12}\,\mathrm{cm}^{-1} \gg 10^{-76}\,\mathrm{cm}^{-1} \approx |\Delta E_{\pm}|/hc \tag{6}$$

With our RPH approach we accurately calculated a torsional tunneling splitting in the two lowest vibrational states of $10^{-12}\,\mathrm{cm}^{-1}$ for a scaled effective torsional potential of $\sqrt{f} \approx 0.17$ without any extrapolation. Thus, de lege symmetry breaking due to parity violation dominates the dynamics of chirality in ClSSCl independently of the detailed accuracy of the extrapolation procedure. Compared to H_2O_2, H_2S_2, and [N-D_1]aniline, which have been recently theoretically classified as belonging to the group of chiral molecules whose molecular chirality is dominated by de facto symmetry breaking,[21–23, 26] the essential difference is a much higher, effective reduced "tunneling mass"[21] and higher barriers against stereomutation in ClSSCl. Thus, the low energy eigenstates of this molecule have a well defined chirality (P or M). If one generates a superposition state of well defined parity (+ or −) by means of the methods proposed in references [2, 19], the value of ΔE_{pv} in ClSSCl corresponds to a period for parity change of about 30 s. The initial time evolution for parity change in the micro- to millisecond range should be measurable by the technique proposed in reference [19]. Vibrational corrections to ΔE_{pv}[27] are small. The modest relativistic corrections[28] are not expected to change our fundamental conclusions. Collisions and superselection rule effects[2, 30–32] also do not change the conclusions on the *relative* importance of $\Delta E_{\pm}$ and ΔE_{pv} derived here, and could be tested in any case by the same type of experiment.[19] We should draw particular attention also to the superselection rule hypothesis of Pfeiffer and Primas,[30, 33] which tries to explain the stabilization of enantiomers in the high barrier limit *without* invoking parity violation, and thus represents an alternative to the present hypothesis using parity violation. The two approaches would predict quite a different outcome for "Quack's experiment" as referred to by Pfeiffer[30] (see also the critical review in reference [2]). Compared to fluorooxirane[29] and methane derivatives such as methane isotopomers[34] or amino acids important for biology[6, 7, 35–40]—all high barrier limit molecules—dichlorodisulfane has the advantage that in addition to parity violation also the stereomutation dynamics is now well understood, providing a new picture of molecular chirality differing fundamentally from Hund's parity-conserving description.[1, 2]

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$[(OC)_5Cr{=}BSi(SiMe_3)_3]$: A Terminal Borylene Complex with an Electronically Unsaturated Boron Atom**

Holger Braunschweig,* Miriam Colling, Carsten Kollann, Klaus Merz, and Krzysztof Radacki

Dedicated to Professor Gerhard E. Herberich on the occasion of his 65th birthday

Stable molecules with both electronically and coordinatively unsaturated boron atoms are extremely rare and restricted to a few methyleneboranes of the type $(Me_3Si)_2C{=}BR$ (R = Me, *t*Bu, 2,3,5,6-tetramethylphenyl, 2,4,6-trimethylphenyl).[1a–e] The chemical and structural properties of such alkyl- and aryl(alkylidene)boranes are decisively determined by the low coordination number and the electron deficiency at the boron center.

A similar bonding situation for boron is found in terminal borylene complexes of the type $[L_xM{=}BR]$ (R = alkyl, aryl, silyl). Owing to their significance[2] for the understanding of metal – boron interactions, alkyl- and arylborylene complexes have been already subject to several theoretical studies.[3a–e] On the basis of ab initio calculations it appears to be generally accepted that these compounds exhibit a stronger metal-to-boron π-backbonding than corresponding borylene complexes $[L_xM{=}B{=}X]$ ($X = NR_2$, F)[4a,b] in which electron deficiency at the boron center is relieved by π interaction with X. Experimental evidence for a complex $[L_xM{=}B{-}R]$ in which R is not a π donor, however, has yet to be reported.

In the course of our investigations on both bridged and terminal borylene complexes,[5a–i] we recently reported on compounds of the type $[(OC)_5M{=}B{=}N(SiMe_3)_2]$ (**1a**, **b**; M = Cr, W). These aminoborylene complexes were obtained either by direct salt elimination reactions[6] or alternatively, in the case of **1a**, by photochemically induced borylene transfer,[7] and represent the only compounds of this type comprising two-coordinate and hence, coordinatively unsaturated boron centers. The boron atom, however, is electronically stabilized by a π-donating amino ligand. Apart from **1a**, **b** only two structurally authentic terminal borylene complexes have been reported, which comprise, however, saturated boron atoms in higher coordination numbers of three and six, respectively.[8, 9]

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