Parity-Violation Effects

Large Parity-Violation Effects in Heavy-Metal-Containing Chiral Compounds**

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The weak neutral current (Z-boson exchange)[1–3] between electrons and nucleons (quarks) introduces a small energy difference (ΔE_{PV}) between enantiomers of a chiral molecule owing to parity violation (P-odd effects).[4,5] There have been several attempts to measure the parity-violation (PV) difference between enantiomers,[6–7] however, such effects are estimated to be of the order of a few millihertz[8–10] for currently known molecules, and several orders of magnitude too low for the present ability of high-resolution spectroscopy. Here we report relativistic calculations of PV effects for several chiral compounds that contain a heavy-metal center; shifts in ΔE_{PV} of up to 4.8×10^{-14} au (300 Hz) are recorded for such compounds as $[(\eta^5\text{-C}_5\text{H}_5)\text{Re(CO)(NO)I}]$, which can easily be prepared. The high ΔE_{PV} value is an indication that future P-odd experiments for chiral molecules should be directed towards heavy-transition-metal complexes.

Since the creation of the unified electroweak theory by Weinberg, Salam, and Glashow, the investigation of PV effects has become one of the most exciting areas in particle physics.[1–3] Precise measurements of PV in atoms are now accurate enough for the standard model to be tested successfully.[11] Electroweak theory also predicts a small energy difference (ΔE_{PV}) between pairs of enantiomers, and thus a breakdown of mirror-image symmetry. The search for such effects currently involves vibrational,[5,12–14] NMR,[15,16] electronic,[17,18] and Mössbauer[6,19] spectroscopy, electric-field optical activity,[20] and preferred crystallization.[21] Most notably, Chardonnet and co-workers performed a saturation spectroscopy experiment for CHFClBr in the 9.3 μm spectral range using a tunable CO_2 laser that provided a spectral purity of 6 Hz.[12] They obtained $\Delta\nu_{PV}=\nu_{R-}-\nu_{S+}=9.4\pm5.1\pm12.7$ Hz between the two enantiomers, where the first value of uncertainty is derived from statistical error and the second is determined by systematic effects. More recently, the same group reduced these uncertainties and obtained $\Delta\nu_{PV}=-4.2\pm0.6\pm1.6$ Hz.[22] Thus the search for the breakdown of mirror-image symmetry in chiral molecules remains one of the most challenging tasks in molecular chemistry and physics.

It is a nontrivial issue to find chiral compounds suitable for high-resolution spectroscopic measurements of parity nonconservation effects.[23] P-odd effects scale approximately like Z^n ($n\approx5$; $Z=$ nuclear charge of the atom),[24] which limits the choice to heavy-element-containing compounds. Furthermore, in accordance with the single-center theorem of Hegstroem, the substance should contain more than one heavy element (either as ligands or chiral centers).[25] A detailed analysis of P-odd effects, with respect to the environment around a center of chirality, has been given by Faglioni and Lazzeretti.[26] Very recently they also proposed the hypothetical molecule [BiHFX] (X = Br, I) as a suitable candidate with PV effects, with the $\Delta\nu_{PV}$ value of the inversion vibrational mode in the Hz range.[27] Here we propose a number of molecules that are known in the literature, each of them containing a heavy-element center leading to large P-odd effects.

The structures of these molecules, as shown in Scheme 1, were fully optimized using density functional theory[28] followed by four-component all-electron Dirac–Fock calculations, which result in an energy shift of $\Delta E_{PV}=2E_{PV}$ for a molecule, as an expectation value of the parity-violation-operator (see Computational Details). Changes in spectroscopic properties ($\Delta\nu_{PV}$) are directly related to $\Delta E_{PV}(\boldsymbol{R})$ (or

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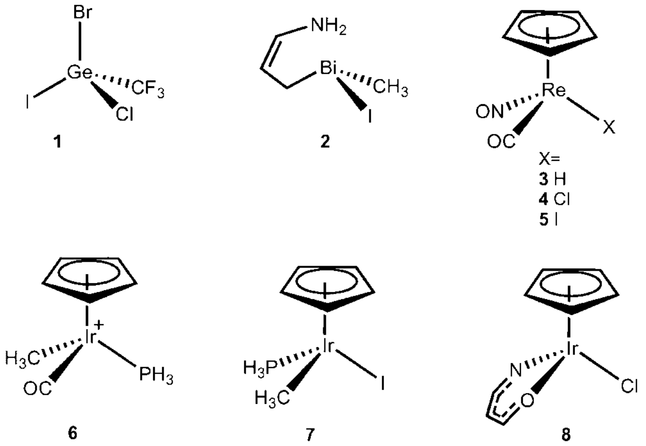
[**] This work was supported by the Alexander von Humboldt Foundation and the Royal Society of New Zealand through a James Cook Fellowship. We are grateful to the Auckland University Research Committee for granting large amounts of computer time.



Scheme 1. The calculated compounds containing chiral metal centers.

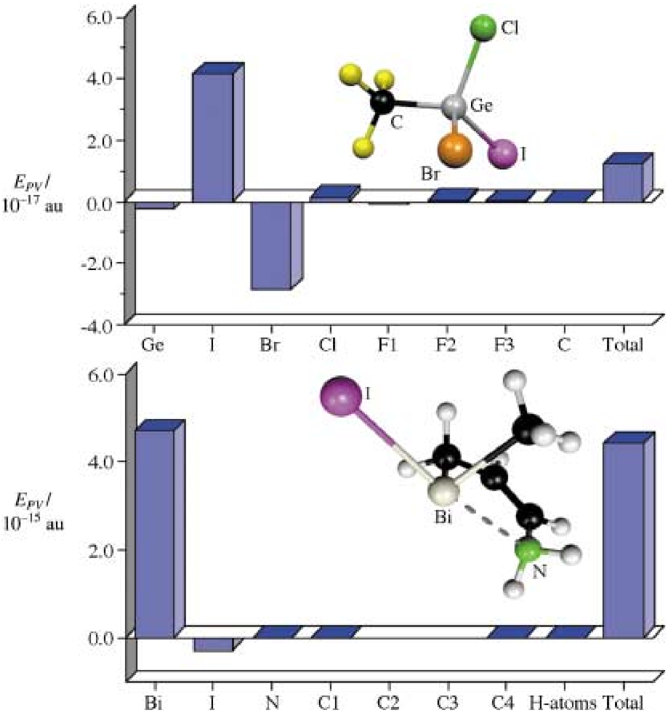


Figure 1. Atomic and total E_{PV} contributions for compounds **1** and **2**.

its derivatives, with respect to the nuclear coordinates $\boldsymbol{R}$), that is, $|\Delta\nu_{PV}| \sim |\Delta E_{PV}|$, and the search for large P-odd effects were therefore initially focused on large $|\Delta E_{PV}|$ values. For example, for a series of chiral carbon compounds, P-odd effects in the C–F stretching mode $(\Delta\nu_{PV}^{\text{C-F}})$ have been examined in detail.[8,23,29] The ratio $|\Delta\nu_{PV}^{\text{C-F}}/\Delta E_{PV}|$ is similar for all such compounds, and ranges between 0.05 and 0.09. Even for the C–Br stretch in CHFBrI, $|\Delta\nu_{PV}^{\text{C-Br}}/\Delta E_{PV}| = 0.09$. By examination, it can be revealed that the major contribution to the E_{PV} value originates from the valence electrons close to the nucleus. This is not unexpected since core orbitals are almost spherical, and hence only contribute to a small degree; or in other words, chirality is revealed in the outer valence shells of a molecule, as one might naively expect.

One of the major problems in the search for P-odd effects in molecules containing main-group heavy elements is to find thermodynamically stable, optically active compounds. For example, [PbHFClBr] displays a $|\Delta E_{PV}|$ value that is more than two orders of magnitude larger than the analogous carbon compound CHFClBr,[8] however, the lead compound, in which the metal center is formally Pb$^{\text{IV}}$, would be easily reduced to give a Pb$^{\text{II}}$ species. There are, however, two relatively stable known chiral compounds: [Ge(CF$_3$)ClBrI] (**1**),[30] which is similar to the already calculated chiral halogen compounds of group 14,[8–10] and [BiCH$_3$I(κ^2-CH$_2$(CH)$_2$NH$_2$)] (**2**), a model compound for a bismuthane species synthesized recently by Murafuji et al.,[31] and similar to the bismuth compound mentioned above.[26] The E_{PV} contributions of the individual atoms are shown in Figure 1 and the total energy shifts ΔE_{PV} are listed in Table 1.

There is no guarantee that values for ΔE_{PV} would reach the current limit of high-resolution spectroscopy once suitable enantiomers containing heavy elements are identified. This is nicely demonstrated for compound **1** where the Ge atom yields only a small PV contribution, while the heavy Br and I ligands show larger effects but of opposite sign and, therefore, cancel each other out; it is currently not known what determines the sign of E_{PV}. The bismuth complex is stabilized by additional coordination of the amino group. Here the total E_{PV} value originates almost entirely from the central Bi atom, which gives a net contribution of $\Delta E_{PV} = 8.88 \times 10^{-15}$ au (58 Hz). Thus, compound **2** is of particular interest for high-resolution spectroscopy.

A large number of thermodynamically stable, optically active heavy-transition-element compounds are known.[32] Of those containing relatively simple ligands are the "piano-stool" compounds containing the C$_5$H$_5^-$ (Cp) ligand, as shown in Scheme 1. To demonstrate the single-center theorem, we varied one of the ligands in the complex [CpRe(CO)(NO)X] (**3**–**5**; X = H, Cl, and I; Figure 2). The value of E_{PV} increases along with an increase in the mass of the ligand X, with X = H giving a negligible contribution of only 1.8×10^{-22} au. Interestingly, the ligand X gives an E_{PV} value of the same sign as the central atom. For the heaviest ligand (I), E_{PV} is of the same order of magnitude as Re, which results in an unprecedented

Table 1: Parity violation energy differences ($\Delta E_{PV} = 2\,E_{PV}$) for the compounds shown in Scheme 1. A negative sign indicates that the enantiomer shown in Scheme 1 is the P-odd-stabilized form.

Compound	ΔE_{PV} [au]	ΔE_{PV} [Hz]
[Ge(CF$_3$)ClBrI] (**1**)	2.466×10^{-17}	0.162
[BiCH$_3$I(κ^2-CH$_2$CHNH$_2$)] (**2**)	8.881×10^{-15}	58.4
[CpReH(CO)(NO)] (**3**)	-2.642×10^{-16}	−1.74
[CpReCl(CO)(NO)] (**4**)	1.752×10^{-14}	115
[CpReI(CO)(NO)] (**5**)	4.807×10^{-14}	316
[CpIr(CO)(CH$_3$)(PH$_3$)]$^+$ (**6**)	-3.525×10^{-14}	−232
[CpIrI(CH$_3$)(PH$_3$)] (**7**)	4.007×10^{-14}	264
[CpIrCl(κ^2-HN(CH)$_3$O)] (**8**)	4.069×10^{-15}	26.8

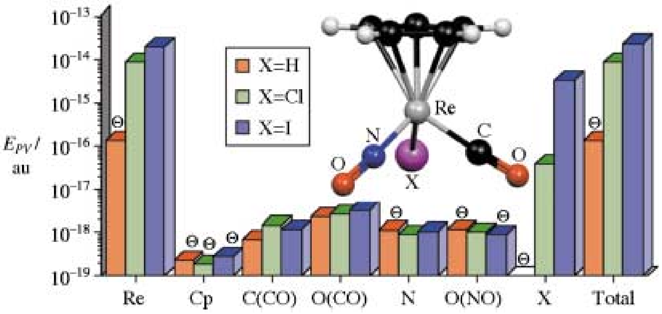


Figure 2. Atomic and total E_{PV} contributions for compounds **3** to **5** shown on the logarithmic scale. Cp denotes all the contributions from the C_5H_5 ligand. If required, the corresponding ligand is given in parentheses along with the coordinate labels of the elements. The label Θ above the bar denotes that E_{PV} is of negative magnitude.

large total value of 2.4×10^{-14} au, which makes compound **5** an ideal candidate for high-resolution measurements.

For the iridium compounds[33–36] studied herein, the main contribution to E_{PV} comes from the central atom. Even for [CpIrI(CH_3)(PH_3)] (**7**) the E_{PV} contribution of iodine (9.5×10^{-16} au) is one order of magnitude below that for the central iridium atom (1.9×10^{-14} au). Table 1 shows that the two isoelectronic compounds [CpIr(CO)(CH_3)(PH_3)]$^+$ (**6**) and [CpIrI(CH_3)(PH_3)] (**7**) show the largest P-odd effect, which are similar in magnitude to the rhenium compound (**5**).

With a few exceptions,[6] the search for P-odd effects in molecules have concentrated on main-group elements.[12,15] In our opinion, transition-metal complexes, especially those of the 6th row, are very good candidates for high-resolution spectroscopy. The compounds investigated here (or some of their derivatives) can be easily synthesized, and the separation of enantiomers may not be as a difficult[37] as it is for the chiral carbon species currently investigated elsewhere.[12,38] We propose high-resolution experiments in both electronic and vibrational spectroscopy for the iridium, rhenium, and bismuth compounds shown in Scheme 1, although current experiments in vibrational spectroscopy are tuned to the CO_2 laser frequency range between 878 and 1108 cm^{-1}.[12] Inclusion of overtones would allow observation of stretching or bending modes in the lower frequency range (450–550 cm^{-1}), which involve transition-metal–ligand stretching modes where larger effects in $\Delta\nu_{PV}$ are expected. Considering electronic transitions, a significant change in P-odd effects from the ground to the excited electronic state is required. It should not be too difficult to identify suitable occupied and unoccupied molecular orbitals by analyzing the matrix elements shown in Equation (1) (see Computational Details), which may result in large changes in $\Delta\nu_{PV}$ for the corresponding electronic transition, for example, excitations involving metal-to-ligand charge transfer. NMR[15] or Mössbauer spectroscopy are also viable alternatives, although in the latter case, strong magnetic fields are required to break the symmetry of Kramers pairs of electrons in a closed-shell system.[6] Here, the use of paramagnetic chiral transition-element compounds is preferred. For theoretical studies of NMR and Mössbauer P-odd effects, the nuclear-spin-dependent parity-violation operator is required. This operator is more difficult to implement into relativistic program packages, as compared to the nuclear-spin-independent operator used here, and work in this direction is in progress.

Computational Details

All structures were fully optimized using the Gaussian 98 program package[28] with scalar relativistic Stuttgart pseudopotentials[39] and corresponding valence basis sets for the heavy elements and cc-pVDZ for the lighter elements at the B3LYP level of theory.[40] Subsequent four-component all-electron Dirac–Fock calculations at optimized geometries[41] gave the energy shift for a molecule with n nuclei and i electrons as an expectation value of the parity-violation operator originating from the time-like contribution of the (A_eV_n) exchange of the weak neutral current between electrons and quarks,[42]

$$\Delta E_{PV} = 2\,E_{PV} = G_F/\sqrt{2}\langle\Psi|\sum\nolimits_{n,i} Q_{w,n}\gamma_i^5\rho_n(\mathbf{r}_i)|\Psi\rangle \qquad (1)$$

where $G_F = 1.6637 \cdot 10^{-11}\ \mathrm{MeV}^{-2} = 2.22255 \times 10^{-14}$ au is the Fermi coupling constant and γ^5 is one of the Dirac matrices (the 4×4 pseudoscalar chirality operator).[28] ρ_n is the normalized nucleon density of nucleus n. The weak charge $Q_{w,n} = -N_n + Z_n(1-4\sin^2\theta_W)$ depends on the number of protons (Z) and neutrons (N), and the Weinberg mixing angle ($\sin^2\theta_W = 0.2319$). Consequently, if one enantiomer becomes stabilized by E_{PV} its mirror image then becomes destabilized by the same amount and we obtain the difference between both enantiomeric forms [Eq. (2)],

$$\Delta E_{PV} = \Delta E_{L\text{-}D} = E_{PV,L} - E_{PV,D} = 2\,E_{PV,L} \qquad (2)$$

For the heavy elements, the dual-type basis sets of Faegri were adopted[43] and double-zeta-quality basis sets with added tight s and p functions for the lighter elements were employed. The Dirac small component was produced by restricted kinetic balance.[44] Because of their expected small contribution, the p orbitals for the hydrogen atoms were omitted, as also were two-electron integrals between small components. For the calculation of the weak charge and in the Dirac–Hartree–Fock calculations, the finite nucleus model of the most stable isotope of each element was used: ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{19}F, ^{35}Cl, ^{74}Ge, ^{79}Br, ^{127}I, ^{187}Re, ^{193}Ir, and ^{209}Bi. Some of these calculations took several weeks of computer time on an IBM Regatta multiprocessor supercomputer. For the compounds shown in Scheme 1 the inversion splitting ($\Delta E_\pm$) arising from a double-minimum potential connecting the two enantiomers is far less than the parity-violation energy difference (ΔE_{PV}) because of the large masses and high barriers involved, that is, $|\Delta E_\pm| \ll |\Delta E_{PV}|$, and inversion splitting can therefore be neglected.[45]

Received: October 25, 2002 [Z50441]

Keywords: ab initio calculations · chirality · density functional calculations · isomerism · parity violation

[1] S. Weinberg, *Rev. Mod. Phys.* **1980**, *52*, 515–523.
[2] A. Salam, *Rev. Mod. Phys.* **1980**, *52*, 525–538.
[3] S. L. Glashow, *Rev. Mod. Phys.* **1980**, *52*, 539–543.
[4] D. W. Rein, *J. Mol. Evol.* **1974**, *4*, 15–22.
[5] V. S. Letokhov, *Phys. Lett. A* **1975**, 53, 275–276.
[6] A. S. Lahamer, S. M. Mahurin, R. N. Compton, D. House, J. K. Laerdahl, M. Lein, P. Schwerdtfeger, *Phys. Rev. Lett.* **2000**, *85*, 4470–4473.
[7] E. Arimondo, P. Glorieux, T. Oka, *Opt. Commun.* **1977**, *23*, 369–372.
[8] J. K. Laerdahl, P. Schwerdtfeger, H. M. Quiney, *Phys. Rev. Lett.* **2000**, *84*, 3811–3814.

[9] M. Quack, J. Stohner, *Phys. Rev. Lett.* **2000**, *84*, 3807–3810.
[10] A. Soncini, A. Ligabue, P. Lazzaretti, R. Zanasi, *Phys. Rev. E* **2000**, *62*, 8395–8399.
[11] A. Derevianko, *Phys. Rev. A* **2002**, *65*, 012106/1–13.
[12] C. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, C. J. Bordé, C. Chardonnet, *Phys. Rev. Lett.* **1999**, *83*, 1554–1557.
[13] O. N. Kompanets, A. R. Kukudzhanov, V. S. Letokhov, L. L. Gervits, *Opt. Commun.* **1976**, *19*, 414–416.
[14] M. Quack, J. Stohner, *Chirality* **2001**, *13*, 745–753.
[15] J. B. Robert, A. L. Barra, *Chirality* **2001**, *13*, 699–702.
[16] M. Fujiki, *Macromol. Rapid Commun.* **2001**, *22*, 669–674; Erratum: M. Fujiki, *Macromol. Rapid Commun.* **2001**, *22*, 864.
[17] L. N. Ivanov, V. S. Letokhov, *J. Chem. Phys.* **1997**, *106*, 6045–6050.
[18] M. Quack, *Chem. Phys. Lett.* **1986**, *132*, 147–153.
[19] A. V. Baluev, L. V. Inzhechik, E. V. Melnikov, B. I. Rogozev, A. S. Khlebnikov, V. G. Tsinoev, V. M. Cherepanov, *JETP Lett.* **1986**, *43*, 656–658.
[20] R. A. Harris, *Chem. Phys. Lett.* **2002**, *365*, 343–346.
[21] A. Szabó-Nagy, L. Keszthelyi, *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 4252–4255.
[22] M. Ziskind, C. Daussy, T. Marrel, C. Chardonnet, *Eur. Phys. J. D* **2002**, *20*, 219–225.
[23] P. Schwerdtfeger, J. K. Laerdahl, C. Chardonnet, *Phys. Rev. A* **2002**, *65*, 042508/1–7.
[24] M. A. Bouchiat, C. Bouchiat, *J. Phys. (Paris)* **1974**, *35*, 899–927.
[25] R. A. Hegstrom, D. W. Rein, P. G. H. Sandars, *J. Chem. Phys.* **1980**, 73, 2329–2341.
[26] F. Faglioni, P. Lazzeretti, *Phys. Rev. E* **2002**, *65*, 011901/1–11.
[27] F. Faglioni, P. Lazzeretti, unpublished results.
[28] Gaussian 98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.
[29] A. Soncini, A. Ligabue, P. Lazzeretti, R. Zanasi, *Phys. Rev. E* **2000**, *62*, 8395–8399.
[30] M. R. Eujen, R. Mellies, *J. Fluorine Chem.* **1983**, *22*, 263–280.
[31] T. Murafuji, K. Satoh, Y. Sugihara, N. Azuma, *Organometallics* **1998**, *17*, 1711–1715; T. Murafuji, N. Azuma, H. Suzuki, *Organometallics* **1995**, *14*, 1542–1544.
[32] H. Brunner, *Angew. Chem.* **1999**, *111*, 1248–1263; *Angew. Chem. Int. Ed.* **1999**, *38*, 1194–1208.
[33] R. P. Hughes, J. M. Smith, L. M. Liable-Sands, T. E. Concolino, K.-C. Lam, C. Invarvito, A. L. Rheingold, *J. Chem. Soc. Dalton Trans.* **2000**, 873–879; R. P. Hughes, D. C. Lindner, J. M. Smith, D. Zhang, C. Invarvito, K.-C. Lam, L. M. Liable-Sands, R. D. Sommer, A. L. Rheingold, *J. Chem. Soc. Dalton Trans.* **2001**, 2270–2278.
[34] S. R. Klei, J. T. Golden, T. D. Tilley, R. G. Bergman, *J. Am. Chem. Soc.* **2002**, *124*, 2092–2093.
[35] P. J. Alaimo, B. A. Arndtsen, R. G. Bergman, *Organometallics* **2000**, *19*, 2130–2143.
[36] M. L. Loza, J. Parr, A. M. Z. Slawin, *Polyhedron* **1997**, *16*, 2321–2322; W. Bauer, M. Prem, K. Polborn, K. Sünkel, W. Steglich, W. Beck, *Eur. J. Inorg. Chem.* **1998**, 485–493.
[37] S. N. Paisner, R. G. Bergman, *J. Organomet. Chem.* **2001**, *621*, 242–245.
[38] D. B. Li, S.-C. Ng, I. Novak, *Tetrahedron* **2002**, *58*, 5923–5926.
[39] The Stuttgart group pseudopotentials and valence basis sets of Stoll and co-workers can be obtained from: http://www.theochem.uni-stuttgart.de/pseudopotentials/.
[40] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.
[41] T. Saue, T. Enveldson, T. Helgaker, H. J. A. Jensen, J. K. Laerdahl, K. Ruud, J. Thyssen, L. Visscher, *Dirac—A relativistic ab initio electronic structure program*, Release 3.2.1, **2000**.
[42] J. K. Laerdahl, P. Schwerdtfeger, *Phys. Rev. A* **1999**, *60*, 4439–4453.
[43] K. J. Faegri, *Theor. Chem. Acc.* **2001**, *105*, 252–258.
[44] I. P. Grant, H. M. Quiney, *Adv. At. Mol. Phys.* **1988**, *23*, 37–86.
[45] M. Quack, *Angew. Chem.* **1989**, *101*, 588–604; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 571–586.

0044-8249/03/11511-1334 $ 20.00+.50/0