Selenium- and Tellurium-Substituted Cyclopropenones and their Facile Ring-Opening with Methanol

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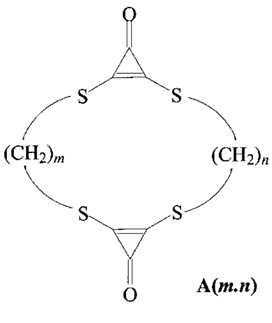
Treatment of donor-substituted acetylenes (X–C≡C–X, with X = R–Se, R–Te) with sodium trichloroacetate, followed by hydrolysis, yielded the corresponding cyclopropenones. Their structures could be elucidated by X-ray analysis, and indicated significant overlap between the p-type lone pairs on the chalcogen atoms and the cyclopropenone unit. DFT calculations were carried out on various conformers in order to clarify their relative energy profiles. Methanolysis of these ring systems at room temperature quantitatively afforded α,β-unsaturated esters.

Introduction

Cyclopropenone and the cyclopropenylium ion are the smallest aromatic species.[1−2] Both systems are distinguished by high strain energies[1−3] and are therefore kinetically labile compounds. The kinetic stability of both ring systems can usually be increased by substitution with electron-donating or bulky groups. The first cyclopropenone derivative reported in the literature was diphenylcyclopropenone.[4] In addition to the synthesis of further aryl- and alkyl-substituted derivatives,[5] cyclopropenones bearing electron-donating substituents such as alkoxy, dialkylamino, and alkylthio groups have also been prepared.[6−7]

We recently reported our investigations on tethered dithiacyclopropenones **A(*m.n*)**, donor-substituted phanes with three-membered π-systems.[8] The structural elucidation of these compounds shows conjugation between the sulfur 3p lone pair and the electron-poor cyclopropenone ring.[8]

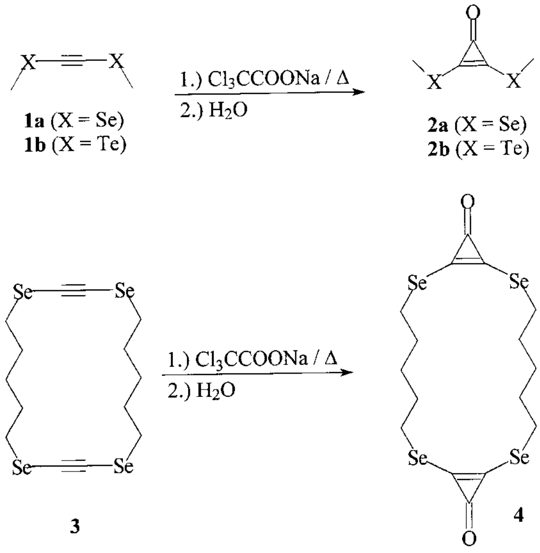


A(*m.n*)

A logical continuation of this research is its extension to heavier chalcogens such as selenium and tellurium as substituents on the cyclopropenone moiety.

Results and Discussion

The starting materials for our syntheses were bis(methylseleno)acetylene[9] (**1a**) and bis(methyltelluro)acetylene (**1b**).[10] Treatment with an excess of dichlorocarbene, generated in situ by thermolysis of sodium trichloroacetate in DME, and subsequent hydrolysis afforded the desired cyclopropenone derivatives **2a** and **2b** in low yields (Scheme 1). Through this reaction we were also able to prepare a tetraselenacyclopropenonophane **4** by starting with a cyclic tetraselenadiyne **3** (Scheme 1).[11]



Scheme 1

Single crystals of **2a** and **2b** were obtained and investigated by X-ray diffraction studies. As an example we show the molecular structure of **2b** in Figure 1. The two cyclopro-

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penone derivatives **2a** and the isomorphous **2b** each adopt a crystallographically imposed C_s symmetry in the solid state.

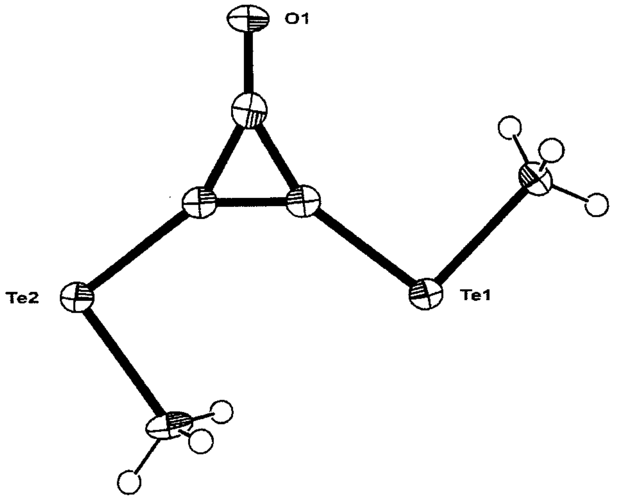
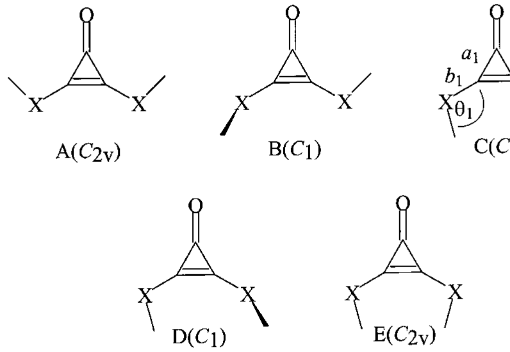


Figure 1. ORTEP plot (50% ellipsoid probability) of the molecular structure of **2b**

We ascribe this behaviour to conjugation between the p-type lone pair on the chalcogen centre and the electron-poor cyclopropenone unit. In order to substantiate this proposal we considered the results of DFT(B3LYP) calculations[12] on chalcogen-substituted cyclopropenones [**2a**, **2b**, **2c** (X = O), and **2d** (X = S)]. Calculations were carried out on five different conformers (A, B, C, D, and E) for each derivative, with the assumption of C_{2v} symmetry for A and E, C_s symmetry for C, and C_1 symmetry for B and D. Table 1 lists the most relevant distances, angles, and torsion angles found in the solid state for **2a** and **2b** compared with those calculated for the C_s-symmetrical conformer C. It is noteworthy that the C−O bond lengths determined in the solid state are about 2 pm longer than the calculated values. A similar effect has previously been observed in sulfur-substituted cyclopropenones.[8]

Table 1. Comparison between selected experimental distances [pm], angles [°], and dihedral angles [°] of **2a** and **2b** with calculated values (for definition see conformer C)

	2a (X-ray)	**2a** (DFT)	**2b** (X-ray)	**2b** (DFT)
C=O	122.1(5)	120.1	122.8(7)	120.2
C=C	136.8(8)	136.2	137.7(7)	136.6
a_1	140.8(6)	143.2	140.4(7)	143.0
a_2	143.0(7)	143.7	142.6(7)	143.6
b_1	186.0(5)	187.5	206.3(5)	206.0
b_2	185.1(5)	187.9	206.4(5)	206.2
θ_1	95.9(2)	98.4	92.3(2)	96.1
θ_2	98.2(2)	96.7	95.8(2)	94.2
C−X−C−C	0.0	0.0	0.0	0.0
	180.0	180.0	180.0	180.0



For each cyclopropenone derivative it was found that conformation A represents the global minimum of the potential surface. C and E are also local minima, while the conformers B and D, which represent transition states from A to C and C to E, respectively, are about 20−27 kJ/mol and 25−30 kJ/mol higher in energy. Table 2 lists exact values for the different conformers, while a graphical representation is given in Figure 2. Natural bond orbital analysis reveals that the magnitude of the rotational barriers is essentially the result of a balance of two effects: (i) the orbital overlap between the lone pairs on the chalcogen atoms and the π* orbital of the cyclopropenone moiety decreases from oxygen to tellurium, and (ii) the energy differential between the orbitals also decreases from oxygen to tellurium. Thus, the sulfur congener shows the highest rotational barrier whereas the tellurium congener shows the lowest.

Table 2. Relative potential energies of chalcogen-substituted cyclopropenones (conformers A−E) in kJ/mol

Conformer	**2c** (X = O)	**2d** (X = S)	**2a** (X = Se)	**2b** (X = Te)
A(C_{2v})	0.0	0.0	0.0	0.0
B(C_1)	22.9	27.1	23.9	20.5
C(C_s)	2.0	3.6	3.8	3.8
D(C_1)	28.5	30.0	27.3	25.0
E(C_{2v})	13.9	15.0	15.0	13.2

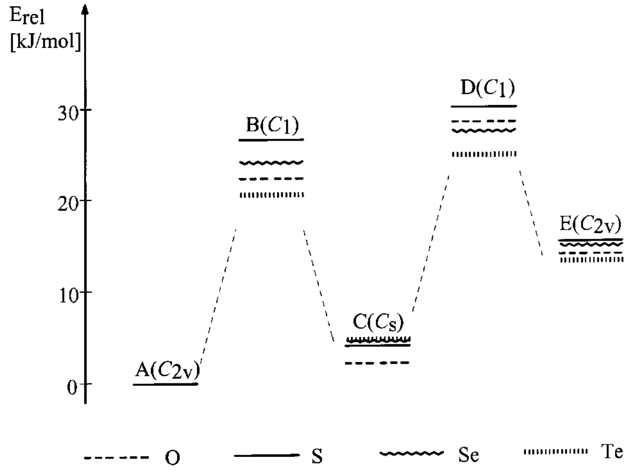
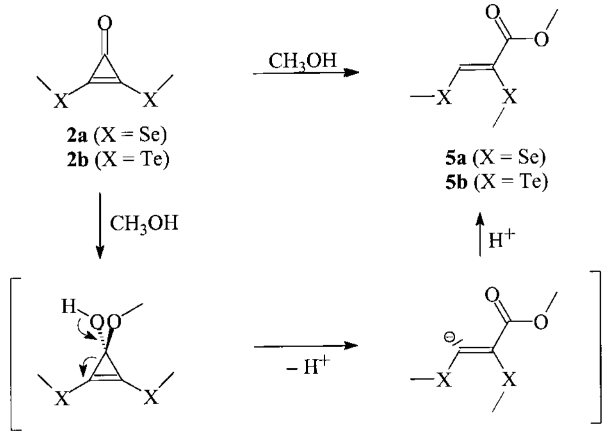


Figure 2. Potential energy diagram of the different conformers A−E (for O, S, Se, and Te)

Treatment of the selenium- and tellurium-substituted cyclopropenones with excess methanol in dichloromethane at room temperature quantitatively afforded the corresponding α,β-unsaturated esters **5a**[13] and **5b** (Scheme 2). No such facile ring-opening reaction is known for alkyl-substituted derivatives, which can be treated with alcohols without decomposition.[14]



Scheme 2

The reaction, also observed with sulfur-substituted cyclopropenones,[15] may be explained as shown in Scheme 2. It is assumed that in the first step the addition of methanol to the highly polarized carbonyl group creates a cyclopropene moiety devoid of any aromatic stabilization. This is followed by the key step, in which the negative charge is placed next to the chalcogen. The better the ability of the chalcogen to stabilize this charge, the more rapidly the ester is formed, the reaction of the tellurium-containing derivative thus taking about twice as long as that of the selenium-substituted one.

In summary, we were able to synthesise the hitherto unknown selenium- and tellurium-substituted cyclopropenones. Their structures were elucidated by X-ray analysis and DFT calculations. A facile ring-opening reaction with methanol to afford α,β-unsaturated esters was discovered.

Experimental Section

General: All reactions were conducted in oven-dried glassware under argon atmospheres with magnetic stirring. DME was dried with sodium/benzophenone and distilled under argon before use. Melting points are uncorrected. Materials used for column chromatography: neutral alumina (Merck) and silica gel (Macherey−Nagel). ^{1}H NMR and ^{13}C NMR: Bruker Avance 300 and Bruker Avance 500 with the solvent as internal standard. IR: Bruker Vector 22 FT-IR. HRMS: JEOL JMS-700. Elemental analyses were carried out by the Mikroanalytisches Laboratorium der Universität Heidelberg. Because of the low yields it was difficult to acquire reliable elemental analytical data for **2b**, **4**, and **5b**. Starting materials **1a**, **1b**, and **3** were prepared by literature methods.[9−11]

General Procedure for the Preparation of Cyclopropenones 2a, 2b, and 4: Sodium trichloroacetate was added stepwise at 50−60 °C, over a period of 2 h, to a solution of the alkyne in DME (120 mL). The reaction mixture was then allowed to cool to room temperature, ethyl acetate (180 mL) was added, and the mixture was cooled to 0 °C. A small volume of water was then added. The phases were separated and the aqueous layer was extracted with dichloromethane. The combined phases were concentrated, and the product was isolated by column chromatography on neutral alumina, eluting with hexane → ethyl acetate (1:0 → 1:1).

Bis(methylseleno)cyclopropenone (2a): Starting materials: bis(methylseleno)acetylene (**1a**, 540 mg, 2.55 mmol) and sodium trichloroacetate (2.40 g, 13.0 mmol) in DME (120 mL). Yield: 43 mg (7%). Colourless solid: m.p. 125 °C (dec.). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.57$ (s, 6 H, C*H*$_3$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): $\delta = 7.7$ (*C*H$_3$), 148.1 (*C*=*C*), 158.8 (*C*=O) ppm. IR (KBr): $\tilde{\nu} = 2930, 1807, 1715, 1482$ cm^{-1}. HRMS (EI, 70 eV): calcd. ($C_5H_6O^{80}Se_2$) 241.8749; found 241.8737. $C_5H_6OSe_2$ (240.02): calcd. C 25.02, H 2.52; found C 25.04, H 2.53. Crystal data: orthorhombic, $a = 10.5120(5)$ Å, $b = 6.8641(1)$ Å, $c = 9.6012(4)$ Å, $V = 692.78(4)$ Å^3, space group *Pnma*, $Z = 4$, $D_c = 2.301$ g·cm^{-3}, $F(000) = 448$, polyhedron, 0.30 × 0.15 × 0.05 mm, $\mu = 10.574$ mm^{-1}, max./min. transmission 1.00/0.51, reflections collected 3513, independent reflections 864, observed reflections 653, $R1 = 0.036$, $wR2 = 0.091$, S(Gof) = 1.12, $(\Delta\rho)_{\max} = 1.25$ e·Å^{-3}, $(\Delta\rho)_{\min} = -0.56$ e·Å^{-3}.

Bis(methyltelluro)cyclopropenone (2b): Starting materials: bis(methyltelluro)acetylene (**1b**, 560 mg, 1.81 mmol) and sodium trichloroacetate (2.34 g, 12.6 mmol) in DME (100 mL). Yield: 25 mg (4%). Brown solid: m.p. 103 °C (dec.). ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.38$ (s, 6 H, C*H*$_3$) ppm. ^{13}C NMR (75.47 MHz, CDCl$_3$): $\delta = -15.0$ (*C*H$_3$), 140.4 (*C*=*C*), 169.4 (*C*=O) ppm. IR (KBr): $\tilde{\nu} = 2921, 1773, 1633, 1428$ cm^{-1}. HRMS (FAB): calcd. ($C_5H_6O^{125}Te^{128}Te$) 336.8664; found 336.8645. Crystal data: orthorhombic, $a = 10.8190(3)$ Å, $b = 7.1394(1)$ Å, $c = 9.9279(3)$ Å, $V = 766.84(3)$ Å^3, space group *Pnma*, $Z = 4$, $D_c = 2.930$ g·cm^{-3}, $F(000) = 592$, polyhedron, 0.14 × 0.08 × 0.06 mm, $\mu = 7.519$ mm^{-1}, max./min. transmission 0.69/0.50, reflections collected 7459, independent reflections 946, observed reflections 770, $R1 = 0.024$, $wR2 = 0.059$, S(Gof) = 1.14, $(\Delta\rho)_{\max} = 0.74$ e·Å^{-3}, $(\Delta\rho)_{\min} = -1.27$ e·Å^{-3}.

1,1′,7,7′-Tetraselena[7,7]cyclopropenophane (4): Starting materials: 1,4,10,13-tetraselenacyclooctadeca-2,11-diyne (**3**, 280 mg, 0.60 mmol) and sodium trichloroacetate (2.80 g, 15.0 mmol) in DME (120 mL). Yield: 23 mg (7%). Colourless solid: m.p. 112 °C (dec.). ^{1}H NMR (500 MHz, CDCl$_3$): $\delta = 1.65$ (quint., 4 H, SeCH$_2$CH$_2$C*H*$_2$), 2.20 (m, 8 H, SeCH$_2$C*H*$_2$), 3.12 (m, 8 H, SeC*H*$_2$) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$): $\delta = 21.8$ (SeCH$_2$CH$_2$*C*H$_2$), 31.1 (SeCH$_2$*C*H$_2$), 33.5 (Se*C*H$_2$), 148.8 (*C*=*C*), 159.8 (*C*=O) ppm. IR (KBr): $\tilde{\nu} = 2922, 1806, 1691, 1487$ cm^{-1}. HRMS (FAB): calcd. ($C_{16}H_{21}O_2{}^{77}Se_2{}^{80}Se_2$) 558.8270; found 558.8268.

General Procedure for the Ring-Opening to α,β-Unsaturated Esters 5a and 5b: Methanol (several mL) was added to a solution of the cyclopropenone in dichloromethane (30 mL). The reaction mixture was stirred at room temperature for 2 days (**5a**) or 5 days (**5b**). The product was purified by column chromatography on silica gel, eluting with hexane/ethyl acetate (1:1).

Ester 5a:[13] Starting materials: bis(methylseleno)cyclopropenone (**2a**, 24 mg, 0.10 mmol). Yield: 26 mg (96%). Yellow oil. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 2.23$ (s, 3 H, SeC*H*$_3$), 2.30 (s, 3 H, SeC*H*$_3$), 3.78 (s, 3 H, OC*H*$_3$), 8.54 (s, 1 H, C=C*H*) ppm. ^{13}C NMR (125.77 MHz, CDCl$_3$): $\delta = 8.0$ (Se*C*H$_3$), 8.0 (Se*C*H$_3$), 52.7 (O*C*H$_3$), 120.0 (*C*=CH), 155.1 (H*C*=C), 164.1 (*C*=O) ppm. IR (film): $\tilde{\nu} =$

3002, 2930, 1706, 1534, 1432 cm^{-1}. HRMS (EI, 70 eV): calcd. ($C_6H_{10}O_2{}^{76}Se^{82}Se$) 271.9040; found 271.9035. $C_6H_{10}O_2Se_2$ (272.06): calcd. C 26.49, H 3.70; found C 26.84, H 3.80.

Ester 5b: Starting materials: bis(methyltelluro)cyclopropenone (**2b**, 19 mg, 0.056 mmol). Yield: 18 mg (88%). Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, TeCH_3), 1.01 (s, 3 H, TeCH_3), 2.61 (s, 3 H, OCH_3), 8.47 (s, 1 H, C=CH) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = −14.6 (TeCH$_3$), −14.3 (TeCH$_3$), 52.9 (OCH$_3$), 113.9 (C=CH), 150.7 (HC=C), 164.8 (C=O) ppm. IR (film): ṽ = 2994, 2945, 1699, 1510, 1430 cm^{-1}. HRMS (EI, 70 eV): calcd. ($C_6H_{10}O_2{}^{128}Te_2$) 369.8788; found 369.8760.

X-ray Diffraction Analyses: The reflections were collected with a Bruker Smart CCD diffractometer (Mo-K_α radiation, graphite monochromator). Intensities were corrected for Lorentz and polarisation effects, and an empirical absorption correction was applied by use of SADABS,[16] based on the Laue symmetry of the reciprocal space. The structures were solved by direct methods. The structural parameters of the non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique (F^2). The hydrogen atoms were calculated according to stereochemical aspects. Structure solution and refinement were carried out with the SHELXTL (5.10) software package.[16] The ORTEP drawing was obtained by use of the ORTEP-3 for Windows program (L. Farrugia).[17] CCDC-190299 (**2a**) and CCDC-190300 (**2b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Details: The geometries of the chalcogen-substituted cyclopropenones were fully optimised with GAUSSIAN98[18] at the density functional level of theory (B3LYP)[12] by use of the split-valence 6-311G* basis set[19] for C, H, O, S, and Se and of the SDB-cc-pVTZ ECP for Te.[20] Frequency calculations were carried out to characterise the nature of the stationary points. The electronic structures were analysed by natural bond orbital (NBO) analysis.

Acknowledgments

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[1] A. Greenberg, R. P. T. Tomkins, M. Dobrovolny, J. F. Liebman, *J. Am. Chem. Soc.* **1983**, *105*, 6855−6858.

[2] P. H. M. Budzelaar, E. Kraka, D. Cremer, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1986**, *108*, 561−567.

[3] H. Dahn, M.-N. Ung-Truong, *Helv. Chim. Acta* **1987**, *70*, 2130−2136.

[4] R. Breslow, R. Haynie, J. Mirra, *J. Am. Chem. Soc.* **1959**, *81*, 247−248.

[5] [5a] T. Eicher, J. L. Weber, *Top. Curr. Chem.* **1975**, *57*, 1−109. [5b] R. Breslow, L. J. Altmann, *J. Am. Chem. Soc.* **1966**, *88*, 504−509. [5c] T. Eicher, N. Pelz, *Tetrahedron Lett.* **1974**, *15*, 1631−1634.

[6] [6a] D. Eggerding, R. West, *J. Am. Chem. Soc.* **1976**, *98*, 3641−3644. [6b] Z. Yoshida, H. Konishi, Y. Tawara, K. Nishikawa, H. Ogoshi, *Tetrahedron Lett.* **1973**, *14*, 2619−2622. [6c] C. Wilcox, R. Breslow, *Tetrahedron Lett.* **1980**, *21*, 3241−3242.

[7] [7a] E. V. Dehmlow, *Chem. Ber.* **1968**, *101*, 410−426. [7b] R. Weiss, C. Schlierf, K. Schloter, *J. Am. Chem. Soc.* **1976**, *98*, 4668−4669.

[8] D. B. Werz, F. Rominger, I. Hyla-Kryspin, R. Gleiter, *J. Org. Chem.* **2001**, *66*, 3416−3422.

[9] A. V. Martynov, G. Le Guillanton, *Bull. Soc. Chim.* **1997**, *134*, 823−831.

[10] R. W. Gedridge Jr., K. T. Higa, D. C. Harris, R. A. Nissan, M. P. Nadler, *Organometallics* **1989**, *8*, 2812−2816.

[11] D. B. Werz, R. Gleiter, F. Rominger, *J. Org. Chem.* **2002**, *67*, 4290−4297.

[12] [12a] A. D. Becke, *J. Chem. Phys.* **1992**, *96*, 2155−2160. [12b] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652. [12c] S. H. Vosko, L. Wilk, M. Nusair, *Cand. J. Phys.* **1980**, *58*, 1200−1211. [12d] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.* **1988**, *37*, 785−789.

[13] The analogous *E* isomer of **5a** has been reported previously: T. Kataoka, M. Yoshimatsu, Y. Noda, T. Sato, H. Shimizu, M. Hori, *J. Chem. Soc., Perkin Trans. 1* **1993**, 121−129.

[14] R. Gleiter, M. Merger, A. Altreuther, H. Irngartinger, *J. Org. Chem.* **1996**, *61*, 1946−1953.

[15] D. B. Werz, R. Gleiter, unpublished results.

[16] G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, WI, **1997**.

[17] Ortep-3 for Windows: A Version of Ortep-III with a Graphical User Interface (GUI): L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[18] *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, Jr., 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, A. G. Baboul, 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. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

[19] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650−654.

[20] [20a] J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408−3420. [20b] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431−1441.

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