Heteroatom Chemistry
Volume 2, Number 4, 1991

X-ray and ^{31}P CP MAS NMR Studies of Bis(dialkoxythiophosphoryl) Disulfides

Marek J. Potrzebowski*

Polish Academy of Sciences, Center of Molecular and Macromolecular Studies, 90-362 Łódź Sienkiewicza 112, Poland

Joseph H. Reinbenspies and Zhiang Zhong

Department of Chemistry, Texas A&M University, College Station, TX 77843, U.S.A.

Received 16 October 1990.

ABSTRACT

The crystal and molecular structures of the title compounds were determined by X-ray diffraction technique from diffractometer intensity measurements. It has been found that two homologous disulfides, bis(dimethoxythiophosphoryl) disulfide **1** *and bis(dineopentoxythiophosphoryl) disulfide* **2**, *form different molecular and crystal structures with space groups* C2/c *and* $P\bar{1}$, *respectively. These results were confirmed by* ^{31}*P CP MAS NMR studies, which showed that under favorable conditions the solid state NMR may lead to determination of the number of crystallographically unique phosphorus atoms. Moreover, the variation of the disulfide S–S bond length versus torsional P–S–S–P angles was observed.*

INTRODUCTION

Interest in the physical and chemical properties of the dithiophosphates [1, 2] has prompted the examination of the bis(dimethoxythiophosphoryl) disulfide **1** and bis(dineopentoxythiophosphoryl) disulfide **2** by single-crystal X-ray diffraction and the solid state ^{31}P cross polarization magic angle spinning NMR spectroscopy. These two experiments provide complementary information into the contents and apparent symmetry of the crystallographic unit cell. Previous workers [3] have utilized the spectra of the powdered samples by ^{31}P CP MAS to determine the number of magnetically nonequivalent ^{31}P nuclei in the asymmetric volume of the unit cell, which under favorable conditions may lead to the determination of the number of crystallographically unique phosphorus atoms. Such information can be of interest in the selection of the correct space group that best describes the arrangement of the molecules in the unit cell.

The assignments of many space groups by inspection of the systematic absences is sometimes ambiguous and the choice often falls to the selection of a centrosymmetric or noncentrosymmetric space group [4]. Methods to distinguish between centrosymmetric or noncentrosymmetric space groups are often difficult to execute or are only sensitive to noncentrosymmetric cases [5, 6]. Such a situation is found with space groups $P1$;$P\bar{1}$ and Cc;$C2/c$. Utilizing solid state ^{31}P CP MAS NMR spectroscopy it may be possible to distinguish between these space groups for samples containing phosphorus atoms by counting the number of crystallographically unique phosphorus atoms in the unit cell and selecting the space group that best describes this result. In this paper we describe the result of these experiments with disulfides **1** and **2**.

EXPERIMENTAL

The synthesis of disulfides **1** and **2** has been previously reported [7]. A colorless crystal (0.16 mm × 0.32 mm × 0.41 mm) of **1** was grown from methanol, and a colorless crystal of **2** (0.20 mm ×

---

*To whom correspondence should be addressed.

1042-7163/91/$3.50 + .25

0.21 mm × 0.41 mm) was grown from hexane/benzene. These crystals were mounted on glass fibers with epoxy in a random orientation at room temperature (formula for **1**: $C_4H_{12}O_4P_2S_4$, $M_r = 314.3$ amu; formula for **2**: $C_{20}H_{44}O_4P_2S_4$, $M_r = 538.7$ amu).

Preliminary examination and data collection for **1** were performed on a Nicolet R3m diffractometer (oriented graphite crystal monochromator, $\lambda(\text{MoK}\alpha) = 0.7107$ Å radiation). Cell parameters for **1** (monoclinic, $a = 21.949(7)$ Å, $b = 10.381(4)$ Å, $c = 12.384(3)$ Å, $\beta = 100.26(3)°$, $V = 2776(2)$ Å^3, $Z = 8$, $D_x = 1.504$ gcm^{-1}, $\mu = 0.874$ mm^{-1}, $F(000) = 1296$ e$^-$) were calculated from the least-squares fitting of the setting angles for 25 reflections. Scan range for data collection was 1.20 plus Kα separation, with variable scan rate of 2.03 to 29.30. Three control reflections collected every 97 reflections showed no significant trends. Background measurement was recorded by stationary crystal and stationary counter technique at the beginning and end of each scan for one-half the total scan time. Lorentz and polarization corrections were applied to 2260 reflections. No absorption correction was applied. A total of 1222 reflections with $|F| \geq 4.0\,\sigma(F)$ were used in further calculations. The structure was solved by direct methods. All nonhydrogen atoms were refined anisotropically; hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 0.08. Full-matrix least-squares refinement yielded $R = 0.0642$ and $R_w = 0.0600$. Neutral scattering factors and anomalous dispersion corrections $\Delta f'$ and $\Delta f''$ were taken from International Tables for X-ray Crystallography [8]. Software for diffractometer control was supplied by Nicolet instrument corporation, and SHELXTL-PLUS [9] was used for structure solution, refinement, and molecular graphics.

The crystal data for **2** were collected using a CAD4 diffractometer with graphite monochromatized Cu-K$_\alpha$ radiation. The crystal was polished to a ball with a diameter of 0.35 mm. Lattice constants were refined by least-square fit of 25 reflections in the θ range 20.35–26.30°. The cell parameters were found to be triclinic, $a = 9.137(1)$ Å, $b = 9.143(2)$ Å, $c = 9.887(2)$ Å, $\alpha = 76.26(2)°$, $\beta = 73.21(1)°$, $\gamma = 82.58(1)°$, $V = 766.4(9)$ Å^3, $Z = 1$, $D_x = 1.167$ gcm^{-1}, $\mu = 39.9$ mm^{-1}, $F(000) = 290$ e$^-$. The structure was solved by the MULTAN program [10], then 2412 observed reflections $I > 4.0\,\sigma(I)$ were used to refine it by full matrix least-squares using F's (8 of the reflections with the biggest difference between F_0 and F_c were rejected before the last cycle of refinement); H atoms were placed at idealized positions with fixed isotropic thermal parameters equal to 1.3 of isotropic thermal parameters that were applied for nonhydrogen atoms. The DIFABS program was used to perform an empirical absorption correction [11]. The refinement converged to $R = 0.097$ and $R_w = 0.099$ with the unit weight for 136 refined parameters; the largest shift/error in the last cycle was 001; the largest residual peak in the final difference Fourier map was 1.48 eÅ^{-3} (near the sulfur atom). All calculations were carried out with the Enraf-Nonius SDP crystallographic computing package.

The systematic absences for **1** narrowed the choice of space group to *Cc* or *C2/c*. For **2** the choice of space groups was *P*1 or *P*$\bar{1}$. Likewise solid state ^{31}P NMR spectroscopy predicted two unique phosphorus nuclei for **1** and one magnetically unique nuclei for **2** [1].

RESULTS AND DISCUSSION

Table of atomic coordinates, bond lengths, and angles are reported in Tables 1 and 2 for disulfide **1** and Tables 3 and 4 for disulfide **2**. Tables of anisotropic thermal parameters, hydrogen atom coordinates, and observed and calculated structure factors are reported in the supplementary materials. The thermal ellipsoidal plots and numbering schemes of disulfides **1** and **2** are shown in Figures 1 and 2, respectively.

Disulfide **1** crystallized in the space group *C2/c* with one molecule per unique volume of the unit cell. As shown in Figure 1 the structure consists of two dimethoxythiophosphoryl moieties bridged by a disulfide unit. The conformations of the phosphoryl groups can be considered gauche (torsional angle P1–S2–S3–P2 = 105.7° (1)). The torsional angles (P1–S2–S3–P2) are larger than those seen for C–S–S–C disulfides [12, 13] and significantly less than those seen for bis(diisopropoxythiophosphoryl) disulfide, as reported elsewhere [14]. The terminal sulfur atoms (S1, S2) are opposed. No unusual bond lengths or angles are seen for the methoxy groups.

Disulfide **2** crystallized in the space group *P*$\bar{1}$ with one-half the molecule per unique volume of the unit cell. As shown in Figure 2 the structure consists of two neopentoxythiophosphoryl moieties bridged by a disulfide unit. The conformations of the phosphoryl groups are trans. As in the case with disulfide **1**, the terminal sulfurs are opposed. No unusual lengths or angles were seen for neopentoxy groups.

As shown in our recent paper the ^{31}P CP MAS NMR spectra for disulfides **1** and **2** revealed that the centerband of disulfide **1** consists of two resonances with $\Delta = 2.98$, whereas the spectrum for disulfide **2** shows a centerband that is a single narrow line [1]. The isotropic shifts were found to be $\delta = 87.10$; $\delta = 84.12$ for **1** and $\delta = 83.99$ for **2**. The two resonances in the spectra of disulfide **1** suggest two nonequivalent phosphorus atoms in the unit volume of the crystallographic unit cell, implying that the centrosymmetric space group *C2/c* is the proper choice of the space group for **1**. Likewise, the single narrow resonance in the spectra of disulfide **2** suggests only one phosphorus atom in the unique volume of the crystallographic unit cell.

TABLE 1 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
P(1)	1284(1)	-1138(2)	3685(2)	60(1)
P(2)	1383(1)	3143(2)	3264(2)	55(1)
S(1)	991(1)	-2417(3)	4568(2)	92(1)
S(2)	701(1)	442(2)	3719(2)	57(1)
S(3)	864(1)	1630(2)	2457(2)	55(1)
S(4)	1406(1)	4456(3)	2202(2)	87(1)
O(1)	1973(2)	-695(6)	4001(5)	88(3)
O(2)	1298(2)	-1436(6)	2441(4)	66(2)
O(3)	1102(2)	3479(6)	4314(4)	64(2)
O(4)	2009(2)	2576(6)	3887(4)	67(2)
C(1)	2263(6)	-529(18)	5129(10)	131(7)
C(2)	769(4)	-1985(13)	1747(7)	85(5)
C(3)	2487(4)	2164(14)	3277(10)	96(5)
C(4)	502(4)	4090(11)	4216(9)	83(5)

P(1)	59(1)	58(2)	61(1)	0(1)	7(1)	3(1)
P(2)	52(1)	55(2)	58(1)	-5(1)	14(1)	-11(1)
S(1)	136(2)	63(2)	78(2)	15(2)	23(2)	-5(2)
S(2)	59(1)	53(2)	64(1)	-1(1)	21(1)	-3(1)
S(3)	57(1)	54(2)	54(1)	-1(1)	6(1)	-8(1)
S(4)	112(2)	67(2)	86(2)	13(2)	28(2)	-22(2)
O(1)	63(4)	92(5)	103(5)	-5(4)	-2(3)	5(4)
O(2)	61(3)	84(5)	54(3)	-13(4)	16(3)	9(3)
O(3)	70(3)	67(4)	59(3)	-8(3)	25(3)	3(3)
O(4)	40(3)	88(5)	71(3)	-9(4)	6(3)	-4(3)
C(1)	113(10)	132(14)	115(9)	-21(12)	-65(8)	-5(10)
C(2)	78(7)	117(11)	60(6)	-29(7)	10(5)	20(7)
C(3)	53(5)	136(11)	107(7)	-16(10)	36(6)	6(7)
C(4)	78(7)	78(9)	100(8)	3(8)	37(6)	24(7)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

TABLE 2 Bond Lengths (Å) and Angles (°) for **1**

P(1)-S(1)	1.904(4)	P(1)-S(2)	2.086(3)
P(1)-O(1)	1.562(6)	P(1)-O(2)	1.576(6)
P(2-S(3)	2.089(3)	P(2)-S(4)	1.901(3)
P(2)-O(3)	1.574(6)	P(2)-O(4)	1.565(5)
S(2)-S(3)	2.071(3)	O(1)-C(1)	1.438(13)
O(2)-C(2)	1.434(10)	O(3)-C(4)	1.446(11)
O(4)-C(3)	1.462(13)		
S(1)-P(1)-S(2)	105.4(2)	S(1)-P(1)-O(1)	118.2(3)
S(2)-P(1)-O(1)	109.5(3)	S(1)-P(1)-O(2)	119.4(3)
S(2)-P(1)-O(2)	107.0(2)	O(1)-P(1)-O(2)	96.7(3)
S(3)-P(2)-S(4)	106.7(1)	S(3)-P(2)-O(3)	107.5(2)
S(4)-P(2)-O(3)	118.4(3)	S(3)-P(2)-O(4)	108.0(2)
S(4)-P(2)-O(4)	118.7(2)	O(3)-P(2)-O(4)	96.7(3)
P(1)-S(2)-S(3)	105.3(1)	P(2)-S(3)-S(2)	103.8(1)
P(1)-O(1)-C(1)	121.3(7)	P(1)-O(2)-C(2)	120.6(5)
P(2)-O(3)-C(4)	120.9(5)	P(2)-O(4)-C(3)	120.2(5)

The space group that best describes this result is the centrosymmetric space group $P\bar{1}$.

The S–S bond length for disulfide **1** (S2–S3 = 2.070(3) is significantly shorter than those seen for disulfide **2** (S2–S2′ = 2.127(2)). The increase in the bond length is directly proportional to the increase in the P–S–S–P torsion angle and follows closely the theoretical calculations for the trans C–S–S–C moieties [13]. It should be stressed that, despite many efforts to rationalize the physico-chemical

TABLE 3 Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å $\times 10^3$) for **2**

	x	*y*	*z*	B(A2) × 10^2
P(1)	2117(2)	3640(2)	3458(2)	394(3)
S(1)	3520(2)	1990(2)	3935(2)	579(5)
S(2)	704(2)	4079(2)	5403(2)	533(5)
O(1)	1060(5)	3461(5)	2508(5)	440(1)
O(2)	2782(5)	5179(5)	2523(4)	420(1)
C(1)	−1958(9)	353(1)	205(1)	960(3)
C(2)	−157(1)	71(1)	236(1)	940(3)
C(3)	12(1)	239(1)	43(1)	960(3)
C(4)	−770(7)	2185(7)	1973(7)	480(2)
C(5)	248(9)	2108(9)	2900(1)	720(2)
C(6)	3919(8)	5800(9)	2947(8)	590(2)
C(7)	4342(7)	7275(7)	1967(7)	430(1)
C(8)	2950(1)	8397(9)	2010(1)	800(3)
C(9)	5030(1)	7080(1)	427(9)	730(2)
C(10)	5580(1)	7890(1)	2440(1)	850(3)

P(1)	51(8)	49.8(8)	49.4(8)	−7.7(6)	−10.5(6)	−12.8(6)
S(1)	74(1)	64(1)	80(1)	8.7(9)	−25.6(9)	−13.9(9)
S(2)	71(1)	73(1)	50.3(9)	2.7(9)	−5.2(8)	−14.4(8)
O(1)	62(2)	50(2)	61(2)	−16(2)	−20(2)	−10(2)
O(2)	56(2)	53(2)	52(2)	−14(2)	−18(2)	−6(2)
C(1)	68(4)	112(7)	211(9)	11(4)	62(5)	−62(6)
C(2)	134(6)	88(6)	151(8)	−40(5)	−59(5)	−8(5)
C(3)	122(7)	168(8)	89(5)	−49(6)	−17(5)	−48(5)
C(4)	61(3)	56(3)	73(4)	−19(2)	−26(3)	−13(3)
C(5)	99(5)	64(4)	126(6)	−19(4)	−58(4)	−7(4)
C(6)	72(4)	79(4)	82(4)	−26(3)	−35(3)	−2(4)
C(7)	54(3)	52(3)	62(3)	−13(2)	−20(2)	−9(3)
C(8)	87(5)	57(4)	164(8)	7(4)	−42(5)	−26(5)
C(9)	109(6)	92(5)	72(5)	−34(4)	−9(4)	−16(4)
C(10)	116(5)	103(6)	129(6)	−28(4)	−61(4)	−23(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) * [*a*2**B*(1,1) + b2**B*(2,2) + *c*2**B*(3,3) + *ab*(cos gamma) **B*(1,2) + *ac*(cos beta)**B*(1,3) + *bc*(cos alpha)**B*(2,3)] The form of the anisotropic displacement parameter is: exp[−2*PI*2{*h*2*a*2*U*(1,1) + *k*2*b*2*U*(2,2) + 12*c*2*U*(3,3) + 2*hkabU*(1,2) + 2*hlacU*(1,3) + 2*klbcU*(2,3)}] where *a*, *b*, and *c* are reciprocal lattice constants.

properties of the disulfide bond, some questions are still a subject of considerable discussion [15, 16], particularly the origin of the relationship between S–S bond length and C–S–S–C torsional angles [17]. Moreover, several research groups have attempted to correlate S–S stretching frequencies with θ(CSSC) and θ(CCSS) in relatively simple model disulfides in the hope that the findings might be extrapolated to the more complicated cystine-containing systems, including proteins [18, 19, 20]. These efforts have achieved only limited success for a number of reasons, in particular due to the lack of suitable models.

Jorgensen and Snyder [21], employing the molecular mechanics approach, have revealed that even for very bulky disulfides the dihedral angle (CSSC) varies in the range 70–114°.

These results for the series of dialkyl disulfides with homogolous increments from dimethyl to the di-*t*-Bu derivative have been confirmed by PES and UV measurements. However, it has been concluded that the release of the steric congestion drives the bulkier disulfides in the direction of the trans geometry. Note that further attempts to search for trans disulfides failed, showing that even for the extremely bulky di-*t*-adamantyl disulfide, the gauche conformation with torsional angle 110° predominates [12].

As seen from data reported here and those published elsewhere [14] the bis(dialkoxythiophosphoryl) disulfides show that the trans geometry is common for the P–S–S–P unit.

In conclusion, although to the best of our knowledge the organophosphorus disulfides have never been considered as models for the studies of the disulfide bond, it seems now that viable models for

TABLE 4 Bond Lengths (Å) and Angles (°) for **2**

P(1)-S(1)	1.912(3)		
P(1)-S(2)	2.079(2)	C(1)-C(4)	1.53(2)
P(1)-O(1)	1.574(6)	C(2)-C(4)	1.53(1)
P(1)-O(2)	1.574(4)	C(3)-C(4)	1.48(2)
S(2)-S(2A)	2.127(2)	C(4)-C(5)	1.47(1)
O(1)-C(5)	1.44(1)	C(7)-C(8)	1.52(2)
O(2)-C(6)	1.45(2)	C(7)-C(9)	1.51(2)
C(6)-C(7)	1.48(1)	C(7)-C(10)	1.55(1)
S(1)-P(1)-S(2)	106.8(1)	C(6)-C(7)-C(8)	111.2(5)
S(1)-P(1)-O(1)	118.4(2)	C(6)-C(7)-C(9)	110.6(6)
S(1)-P(1)-O(2)	118.6(2)	C(6)-C(7)-C(10)	108.3(6)
S(2)-P(1)-O(1)	107.7(2)	C(8)-C(7)-C(9)	108.7(7)
S(2)-P(1)-O(2)	107.1(2)	C(8)-C(7)-C(10)	110.3(7)
O(1)-P(1)-O(2)	97.5(2)	C(9)-C(7)-C(10)	107.8(6)
P(1)-O(1)-C(5)	118.6(5)	O(1)-C(5)-C(4)	111.2(7)
P(1)-O(2)-C(6)	118.5(4)	O(2)-C(6)-C(7)	109.9(6)
P(1)-S(2)-S(2)	99.6(1)		
C(1)-C(4)-C(2)	110.0(6)		
C(1)-C(4)-C(3)	105.8(7)		
C(1)-C(4)-C(5)	112.7(8)		
C(2)-C(4)-C(3)	107.0(8)		
C(2)-C(4)-C(5)	110.6(7)		
C(3)-C(4)-C(5)	110.5(7)		

studies of the stable conformations of disulfides at range 0–180° are at hand.

ACKNOWLEDGMENTS

The authors are grateful to Prof. J. Michalski (PAS) and Prof. A. I. Scott (TAMU) for interest of this project, to Dr. P-J Chu (TAMU) and to Dr. M. Wieczorek (Technical University Łódź) for helpful discussion, and to the Polish Academy of Sciences for support (grant MR-I-12).

SUPPLEMENTARY MATERIALS AVAILABLE

The crystallographic data, tables of anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and structure factors for **1** and **2** are deposited at the Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, United Kingdom.

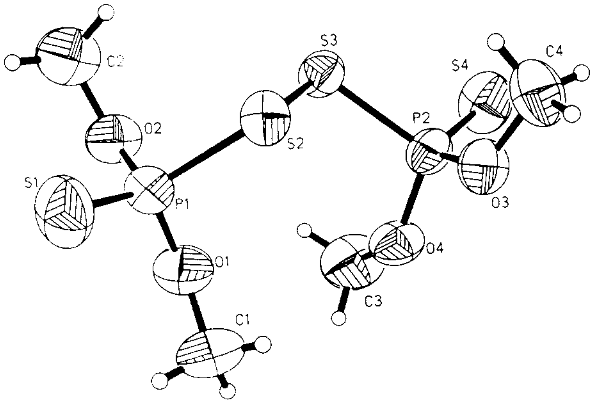

FIGURE 1 Thermal Ellipsoidal Plot (50% probability) and the Numbering Scheme of **1**.

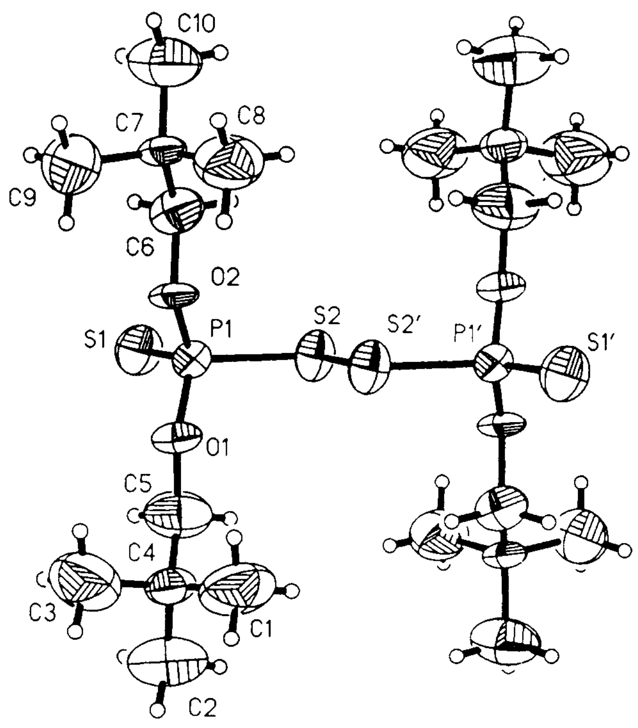

FIGURE 2 Thermal Ellipsoidal Plot (50% probability) and the Numbering Scheme of **2**.

REFERENCES

[1] P. J. Chu, M. J. Potrzebowski, *Magn. Res. Chem.*, *28*, 1990, 477, and references cited therein.

[2] J. Michalski, A. Łopusinski, B. Jezierska, L. Łuczak, M. Potrzebowski, *Phosphorus and Sulfur*, *30*, 1987, 221.

[3] R. K. Harris, L. H. Merwin, G. Hagele, *J. Chem. Soc. Faraday Trans. I*, *83*, 1987, 1055.

[4] A. Voss, M. J. Buerger: *International Tables for X-ray Crystallography*, Vol. A. pp. 39–48 (1987).

[5] T. Hahn, M. Klapper: *International Table for X-ray Crystallography*, Vol. A. pp. 786–791 (1987).

[6] M. J. Buerger: *Elementary Crystallography*, New York, Wiley and Sons, pp. 183–191 (1956).

[7] *Methoden der Organische Chemie* (Houben-Weyl), XII/2,613, Georg Thieme Verlag, Stuttgart, 1964.

[8] D. T. Cromer, J. T. Waber: *International Tables for X-ray Crystallography*, Vol. IV, Birmingham, Kynoch Press, pp. 55–59 (1974).

[9] G. M. Sheldrick: *SHELXTL-PLUS*, revision 3.4, Nicolet Instrument Corporation, 1988.

[10] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P Declercq, M. M. Woolfson: *MULTAN 80: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, University of York, England, and University of Louvain, Belgium, 1980.

[11] N. Walker, D. Stuart, *Acta Crystallogr. Sect.*, *A39*, 1983, 159.

[12] F. S. Jorgensen, J. P. Snyder, *J. Org. Chem.*, *45*, 1980, 1015.

[13] M. Ohsaku, N. Allinger, *J. Phys. Chem.*, *92*, 1988, 4591.

[14] S. L. Lawton, *Inorg. Chem.*, *9*, 1970, 2269.

[15] G. Rindorf, F. S. Jorgensen, J. P. Snyder, *J. Org. Chem.*, *45*, 1980, 5343.

[16] H. G. Guttenberger, H. J. Bestmann, F. L. Dickert, F. S. Jorgensen, J. P. Snyder, *J. Amer. Chem. Soc.*, *103*, 1981, 159.

[17] O. Knop, R. J. Boyd, S. C. Choi, *J. Amer. Chem. Soc.*, *110*, 1988, 7299.

[18] H. E. Van Wart, A. Lewis, H. A. Scheraga, F. D. Saeva, *Proc. Natl. Acad. Sci. USA*, *70*(9), 1973, 2619.

[19] H. E. Van Wart, L. L. Shipmann, H. A. Scheraga, *J. Phys. Chem.*, *78*, 1974, 1848, and references cited therein.

[20] W. Zhao, J. Bandeker, S. Krim, *J. Amer. Chem. Soc.*, *110*, 1988, 6891.

[21] F. S. Jorgensen, J. P. Snyder, *Tetrahedron*, *35*, 1979, 1399.