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Note

Fluorine-substituted tetraazaannulene complexes: syntheses and characterizations

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Abstract

The syntheses of two new fluorine-substituted tetraazaannulene macrocyclic complexes have been accomplished. A mixture of the *cis*- and *trans*-bis(trifluoromethyl) substituted macrocycles, 5,7-bis(trifluoromethyl)-12,14-dimethyldibenzo[*b,i*][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(*cis*-BTDMTAA)], and 5,12-bis(trifluoromethyl)-7,14-dimethyldibenzo[*b,i*][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(*trans*-BTDMTAA)], results in low yield from the reaction of 1,1,1-trifluoro-2,4-pentanedione and 1,2-diaminobenzene in the presence of nickel(II) acetate tetrahydrate. The two one-electron oxidations observed for the corresponding Ni(II) complex of the tetramethyltetraazaannulene are shifted to significantly more positive values (+0.85 and +1.15 V). The macrocyclic complexes do not display the characteristic electropolymerization of other tetraazaannulenes, which suggests that the second oxidation is not associated with the oxidation of a coupled dimer. The bis(trifluoromethyl) derivatives do bind CO_2 in solution and catalyze the electrochemical reduction to formate. The reduction occurs at −1.06 V, almost 0.5 V more positive than the value observed for the electropolymerized tetramethyl complex. An octafluorotetramethyltetraazaannulene, prepared by the reaction of 3,4,5,6-tetrafluoro-1,2-diaminobenzene with 2,4-pentanedione, is also reported.

Keywords: Nickel complexes; Multidentate ligand complexes; Tetraazaannulene complexes

1. Introduction

Interest in recent years has centered on macrocyclic complexes [1] as bioinorganic mimics for metal sites in proteins [2] and as highly stable complexes for catalytic materials [3]. The flexibility afforded by various organic structures has allowed the chemist to fine-tune the electronic properties of coordinated metals [4]. Thus, a number of bioinorganic model complexes have been prepared with metals that possess a range of coordination properties or redox potentials.

One class of macrocyclic ligands that we have considered in some detail is the tetraazaannulenes. These ligands (Fig. 1) have proven to be particularly interesting, since they are relatively easy to prepare, by use of the template effect, using Ni as the template metal [5]. They have also been proposed as models for porphyrins.

Unlike the porphyrins, however, these ligands form complexes that are sometimes nonplanar [6–9], often saddle-shaped such that extensive electron delocalization, known to occur in the porphyrins, occurs only in the three-carbon chain. Recently, we undertook the synthesis and characterization of a number of tetraazaannulene complexes [10–12]. The complexes investigated include those with $R_1 = H$, Me, Et, Ph. In addition, we reported the novel observation that ligands with small substituents undergo electropolymerization on the surface of an electrode, at the first oxidation potential observed for the ligand [13]. That process has been studied extensively and is now well understood

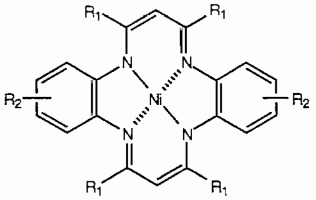

Fig. 1. Lewis structure of an Ni(II) tetraazaannulene macrocycle similar to those studied in this work.

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for a number of metals and substituted ligands. Deronzier and Marques recently re-investigated the electrochemical behavior of Cu(II) and Ni(II) complexes of these tetraazaannulenes and have described in more detail the unique features of the cyclic voltammograms observed [14,15]. In addition to the extensive studies of the polymerization process, we have reported the synthesis of the very bulky (R_1 = Ph) tetraphenyl-tetraazaannulene and that this complex does not polymerize on the surface of an electrode [12].

Perhaps even more interesting, however, was the observation that the Ni(II) complex of tetraazaannulene with R = Me catalyzes the electrochemical reduction of CO_2 on an electrode surface [16]. In that experiment, an electrode surface, when coated with the electropolymerized macrocyclic complex, bound and activated CO_2 for electrochemical reduction at a potential far less than that for dissolved CO_2. The only product of this reduction was formate ion, HCO_2^-, as determined by ^{13}C NMR [16]. In addition, a number of other substrates have been shown to undergo catalyzed electrochemical reductions with a variety of metal-substituted tetraazaannulenes [10,12].

Recently, Ellis and Lyons reported that fluorine substitution in iron porphyrins dramatically increased the catalytic activity of these complexes [17,18]. In addition, they reported that these complexes possessed greater oxidative stability than their nonfluorinated counterparts. We have chosen to undertake a study of fluorine-substituted tetraazaannulenes to determine if the fluorine-substituted complexes could be prepared, and if so, whether these complexes undergo electropolymerization. Finally, it was of interest to determine if fluorine substitution enhanced the electrocatalytic reduction of CO_2.

2. Experimental

2.1. General

^1H NMR spectra were obtained at 300.075 MHz on a Varian Gemini 300 NMR spectrometer; chemical shifts are reported in ppm downfield from tetramethylsilane, using the peak for $CDCl_3$ (7.26 ppm) as a reference. ^{19}F NMR spectra were obtained at 282.33 MHz on a Varian Gemini 300 NMR spectrometer; chemical shifts are reported in ppm downfield from internal $CFCl_3$ (0 ppm) as a reference. High resolution mass spectra were obtained on a JEOL HX110HF mass spectrometer using electron impact ionization.

1,2-Diaminobenzene, nickel(II) acetate tetrahydrate, and 1,1,1-trifluoro-2,4-pentanedione were obtained from Aldrich and used as received. Absolute ethanol was obtained from Midwest Grain Products and used as received. Methylene chloride, hexanes, ethyl acetate and alumina were obtained from Fisher and used as received. Acetonitrile (Fisher) was distilled from calcium hydride and used immediately or stored over 4 Å molecular sieves until use. Carbon dioxide was obtained from Matheson Gas Products and used as received.

Electrochemical measurements were determined in methylene chloride solution at analyte concentrations of 5×10^{-3} M, with 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Cyclic voltammograms were obtained using a Bioanalytical Systems CV-27 potentiostat and recorded using a YEW model 3022 A4 X–Y recorder. The measurements were made using a Bioanalytical Systems platinum disk (2 mm) working electrode versus a saturated calomel electrode, with a platinum wire employed for the auxiliary electrode. Before use, the disk electrode was polished sequentially with 1 and 0.25 μm diamond paste (Buehler) on a Buehler nylon disk, followed by ultrasonic cleaning in deionized water (5 min) and in acetonitrile (5 min). Solutions were degassed with Ar for 15 min prior to use.

2.2. Syntheses

2.2.1. 5,7-Bis(trifluoromethyl)-12,14-dimethyldibenzo-[b,i][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(cis-BTDMTAA)], and 5,12-bis(trifluoromethyl)-7,14-dimethyldibenzo[b,i][1,4,8,11]-tetraaza[14]-annulene nickelate, [Ni(trans-BTDMTAA)]

1,2-Diaminobenzene (2.70 g, 25.0 mmol) and nickel(II) acetate tetrahydrate (3.23 g, 13.0 mmol) were dissolved in absolute ethanol (50 ml) and the mixture refluxed for 30 min. 1,1,1-Trifluoro-2,4-pentanedione (3.1 ml, 3.9 g, 26 mmol) was added and the resulting mixture refluxed for 12 h. The solvent was removed in vacuo and the residue was taken up into methylene chloride (25 ml). The solution was filtered to remove any solids and applied to an alumina column using methylene chloride as eluent. The fast-moving green band was collected and evaporated to dryness to give a dark green solid. This solid was applied to a preparative thin-layer chromatography (TLC) plate using hexanes/ethyl acetate (90/10) as eluent to give two green bands, which were removed from the plate and washed with methylene chloride (50 ml).

2.2.2. 5,7-Bis(trifluoromethyl)-12,14-dimethyldibenzo-[b,i][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(cis-BTDMTAA)]

The solvent from the first band was removed in vacuo to give 4.0 mg (0.13%) of Ni(*cis*-BTDMTAA) as a green solid; m.p. 273–275 °C. ^1H NMR: δ 2.11 (s, 6H), 5.41 (s, 2H), 6.68 (m, 8H); ^{19}F NMR: δ −59.3 (s). Exact mass calc. for $C_{22}H_{16}F_6N_4Ni$ (M^-): 508.0633; found: 508.0647.

2.2.3. 5,12-Bis(trifluoromethyl)-7,14-dimethyldibenzo-[b,i][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(trans-BTDMTAA)]

The solvent from the second band was removed in vacuo to give 13 mg (0.41%) of Ni(*trans*-BTDMTAA) as a green solid; m.p. 297–299 °C. ^1H NMR: δ 2.11 (s, 6H), 5.40 (s, 2H), 6.55 (m, 4H), 6.70 (m, 4H); ^{19}F NMR: δ −59.7 (s). Exact mass calc. for $C_{22}H_{16}F_6N_4Ni$ (M^-): 508.0633; found: 508.0620.

2.2.4. 2,3,4,5-Tetrafluoro-6-nitroaniline

2,3,4,5-Tetrafluoro-6-nitroaniline was synthesized according to the method of Tatlow and co-workers [19]. Pentafluoronitrobenzene (5.00 ml, 5.31 g, 24.9 mmol) was dissolved in diethyl ether (150 ml), and anhydrous ammonia was bubbled through the resulting solution. Completion of the reaction was noted by following the disappearance of pentafluoronitrobenzene by TLC ($R_f = 0.90$ with toluene as eluent, reaction time approximately 2.5 h). After the reaction was complete, the solution was filtered and the diethyl ether was evaporated in vacuo. The residue was dissolved in toluene and applied to an alumina column using toluene as eluent. The first band off the column was collected and the solvent removed to give 2.67 g (51%) of 2,3,4,5-tetrafluoro-6-nitroaniline as a bright yellow solid. The product identity was confirmed and the purity determined to be ≥99% by ^1H and ^{19}F NMR. ^1H NMR: δ 5.79 (s, br); ^{19}F NMR: δ −145.2 (m), −147.6 (m), −160.7 (m), −172.6 (m) (lit. [19] −146.8, −150.0, −159.8, −175.5).

2.2.5. 3,4,5,6-Tetrafluoro-1,2-diaminobenzene

3,4,5,6-Tetrafluoro-1,2-diaminobenzene was synthesized by the reduction of 2,3,4,5-tetrafluoro-6-nitroaniline using zinc and acetic acid. 2,3,4,5-Tetrafluoro-6-nitroaniline (2.67 g, 14.8 mmol) was dissolved in a mixture of methanol (50 ml) and glacial acetic acid (25 ml). To this stirring solution, zinc dust was added in small (≈ 0.5 g) portions until no 2,3,4,5-tetrafluoro-6-nitroaniline remained. Completion of the reaction was noted by following the disappearance of 2,3,4,5-tetrafluoro-6-nitroaniline by TLC ($R_f = 0.85$ with methylene chloride as eluent). The methanol was removed using rotary evaporation, and the remaining solution was dissolved in methylene chloride (200 ml). The resulting mixture was extracted with saturated sodium carbonate solution (5×200 ml). The organic layer was removed, dried over anhydrous magnesium sulfate, and the solvent was removed in vacuo to give 2.46 g of crude product. The crude product was recrystallized from benzene to give 1.95 g (85%) of 3,4,5,6-tetrafluoro-1,2-diaminobenzene as a dark purple solid. The product identity was confirmed and the purity determined to be ≥99% by ^1H and ^{19}F NMR. ^1H NMR: δ 3.41 (s, br); ^{19}F NMR: δ −162.6 (m), −172.2 (m) (lit. [19] −163.6, −175.8).

2.2.6. 15,16,17,18,19,20,21,22-Octafluoro-5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]-tetraaza[14]annulene nickelate, [Ni(OFTMTAA)]

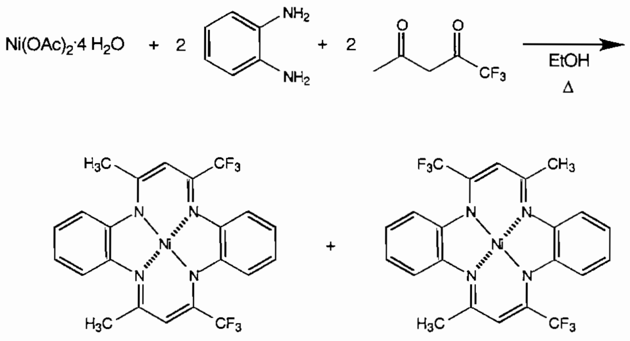
3,4,5,6-Tetrafluoro-1,2-diaminobenzene (330 mg, 1.83 mmol) and nickel acetate tetrahydrate (225 mg, 0.91 mmol) were dissolved in absolute ethanol (25 ml) and stirred at 70 °C for 6 h. 2,4-Pentanedione (0.19 ml, 0.185 g, 1.85 mmol) was added and the resulting mixture was refluxed for 12 h. The solvent was removed in vacuo and the residue was taken up into methylene chloride (25 ml). The solution was filtered to remove any solids and applied to an alumina column using methylene chloride as eluent. The fast-moving greenish-brown band was collected and evaporated to dryness to give a dark brown solid. This solid was applied to a preparative TLC plate using hexanes/ethyl acetate (90/10) as eluent to give a fast-moving greenish-brown band, which was removed from the plate and washed with methylene chloride (50 ml). The solvent was removed in vacuo to give 1.5 mg (0.34%) of Ni(OFTMTAA) as a dark greenish-brown solid; m.p. 134–137 °C. Exact mass calc. for $C_{22}H_{14}F_8N_4Ni$ (M^-): 545.0766; found: 545.0761.

3. Results and discussion

3.1. Ni(cis-BTDMTAA) and Ni(trans-BTDMTAA)

3.1.1. General

The *cis* and *trans* isomers of the bis(trifluoromethyl)-substituted tetramethyltetraazaannulene have been synthesized as their nickel(II) complexes (Scheme 1) in very low yield. This was achieved by heating a mixture of 1,2-diaminobenzene, 1,1,1-trifluoro-2,4-pentanedione and nickel acetate in ethanol. Although yields of tetramethyltetraazaannulene macrocycles are sometimes low, we have found the yields of these fluorinated macrocycles to be extremely poor. The yields can be attributed to the use of a trifluoromethyl ketone as a



Scheme 1. Synthesis of Ni(*cis*-BTDMTAA) and Ni(*trans*-BTDMTAA).

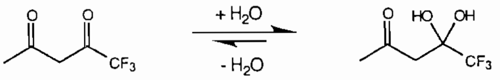
starting dione. Trifluoromethyl ketones have been shown to form hydrates quite easily, although it is generally considered to be an equilibrium process (Scheme 2). Initially, we considered the water of hydration of nickel(II) acetate to be a problem, since the formation of ketone hydrate would greatly diminish the electrophilicity of the carbonyl carbon. However, the use of anhydrous sources of nickel(II) did not change the yields significantly. This suggests that the solvent, ethanol, may play a part in the low yields by the formation of a hemi-acetal, which would behave similarly to a hydrate. Attempts to increase the yield of this synthesis in other solvents met with no success, since we did not find another suitable solvent for the Ni(II) starting material.

Separation of the mixture of isomers from the remainder of the reaction mixture was achieved readily. However, identification of the isomers was not possible. Once the two isomers were separated, it was found that one isomer was formed in approximately a 3:1 ratio over the other.

Assignment of the isomers is not possible by examining the ^1H NMR spectra. However, it is well known that the trifluoromethyl group behaves sterically much like an isobutyl (or larger) group [20–22]. Thus, we feel it is reasonable that the major isomer is assigned as being the *trans* isomer, based on the need to minimize steric interactions with the aromatic rings. In addition, MM2 calculations [23] carried out on these macrocyclic systems show that the *trans* isomer is approximately 7 kcal mol^{-1} more stable than the *cis* isomer. We have not been able to grow a single crystal suitable for X-ray crystallographic analysis at this time.

3.1.2. *Electrochemistry*

The cyclic voltammograms of Ni(*cis*-BTDMTAA) (Fig. 2) and Ni(*trans*-BTDMTAA) are identical, and show that the bis(trifluorinated) macrocycle exhibits reversible, one-electron redox waves at +0.85 and +1.15 V. These oxidation waves are significantly more positive than those of the nonfluorinated counterpart, 5,7,12,14-tetramethyldibenzo[*b*,*i*][1,4,8,11]-tetraaza[14]annulene nickelate, NiTMTAA ($E^1_{1/2}=0.42$ V and $E^2_{1/2}=0.97$ V) [24]. It is especially interesting to note that a reduction wave is not visible for either isomer, as is observed for all other Ni(II) examples of this substituted complex we have studied.



Scheme 2. The formation of the trifluoromethyl ketone hydrate of 1,1,1-trifluoro-2,4-pentanedione.

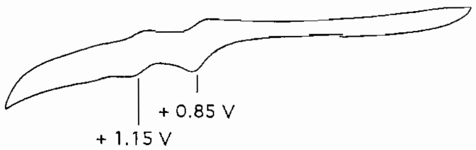


Fig. 2. Cyclic voltammogram of Ni(*cis*-BTDMTAA).

One of the goals of this work was to incorporate the fluorine-substituted macrocycle into a polymeric thin film and explore its catalytic ability, as described previously [13]. Attempts to polymerize either isomer of Ni(BTDMTAA) by scanning repeatedly over both of the reversible oxidation waves did not show an increase in the current passed, indicating that neither isomer of Ni(BTDMTAA) undergoes the electrochemical polymerization reaction.

Earlier work [13] has shown that the polymerization takes place via the coupling of radicals on the carbon atoms that were formerly the carbon atoms between the carbonyl moieties on the pentanedione derivative. As radicals are electron-deficient species, it might be expected that the presence of the trifluoromethyl group would make the formation of a radical on a carbon two atoms away energetically unfavorable. Therefore, upon oxidation of these complexes, it is expected that any radicals formed would reside far from the trifluoromethyl group, most likely on the aromatic rings. Molecular orbital (MO) calculations using the ZINDO method confirmed this suggestion, indicating that neither the singly nor the doubly oxidized Ni(II) tetraazaannulene complex possesses any significant radical character at the central carbon of the bridge.

Despite the inability to form polymeric thin films, the electrocatalytic reduction of CO_2 remained of great interest. After an acetonitrile solution containing either Ni(*cis*-BTDMTAA) or Ni(*trans*-BTDMTAA) was saturated with CO_2, a cyclic voltammogram revealed a large, irreversible reduction wave at −1.06 V (Fig. 3). The location of this wave was the same for each of the two isomers, and great care was taken to ensure the reproducibility of this result. This observation seems remarkable. The reduction potential for the CF_3-substituted complexes has moved to a value almost 1 V

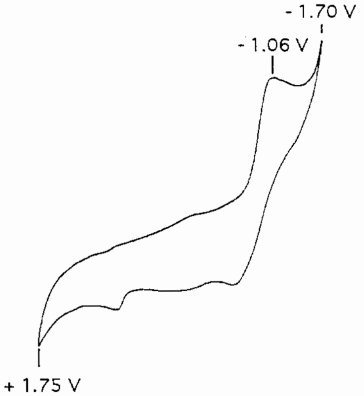
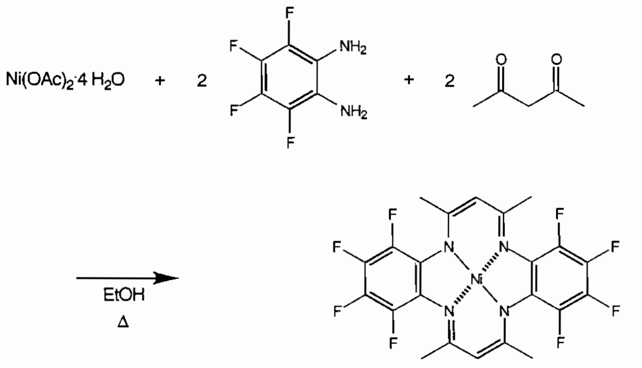


Fig. 3. Cyclic voltammogram of a CO_2 saturated solution of Ni(*trans*-BTDMTAA), showing the irreversible reduction at −1.06 V.



Scheme 3. Synthesis of Ni(OFTMTAA).

more positive than that for free CO_2 in solution, and almost 0.5 V more positive than that for the CH_3 derivative. These molecules seem to offer promise as a portion of a catalytic system for the reduction of CO_2. Further work in this area is in progress in our laboratory.

3.2. Ni(OFTMTAA)

Ni(OFTMTAA) has been synthesized (Scheme 3) via the template condensation of 3,4,5,6-tetrafluoro-1,2-diaminobenzene with 2,4-pentanedione in the presence of nickel(II) acetate. Difficulties associated with the purification of the 3,4,5,6-tetrafluoro-1,2-diaminobenzene, combined with an exceedingly low yield, prevented the synthesis of large enough quantities to perform a complete characterization. The low yields result in part because of the decreased nucleophilicity of the fluorinated amine. However, the mass spectral data confirm the isolation of the target molecule. The electrochemistry of Ni(OFTMTAA) appears only as a single irreversible oxidation at +1.40 V.

4. Conclusions

Several fluorinated derivatives of the macrocyclic complex NiTMTAA have been synthesized in very low yields. Two bis(trifluoromethyl)-substituted macrocycles, Ni(*trans*-BTDMTAA) and Ni(*cis*-BTDMTAA), have been synthesized as a mixture of isomers in a 3:1 ratio and characterized using NMR and cyclic voltammetry. The assignment of *cis* and *trans* isomers is based on the expectation that the less sterically strained *trans* isomer would be formed preferentially over the *cis* isomer. It was found that both isomers exhibit the same electrochemical properties, including the apparent facilitation of the reduction of CO_2. The catalytic reduction of bound CO_2 was found to occur at −1.06 V, nearly 0.5 V more positive than the value for the reaction on a surface-modified electrode containing a thin film of the parent macrocycle. This value is also almost one full volt more positive than the approximately −2 V necessary for the reduction of unbound CO_2.

References

[1] W. Küster, *Z. Physiol. Chem., 82* (1912) 463.
[2] D.H. Busch, K. Farmery, V. Goedken, V. Katovic, A.C. Melnyk, C.R. Sperati and N. Tokel, *Adv. Chem. Ser., 100* (1971) 44.
[3] E.C. Niederhoffer, J.H. Timmons and A.E. Martell, *Chem. Rev., 84* (1984) 137.
[4] (a) D.K. Cabbiness and D.W. Margerum, *J. Am. Chem. Soc., 91* (1969) 6540; (b) *92* (1970) 2151.
[5] D.H. Busch, *Adv. Chem. Ser., 37* (1973) 1.
[6] V.L. Goedken, J. Molin-Case and Y.-A. Whang, *J. Chem. Soc., Chem. Commun.*, (1975) 337.
[7] V.L. Goedken, J.J. Pluth, S.-M. Peng and B. Bursten, *J. Am. Chem. Soc., 98* (1976) 8014.
[8] M.C. Weiss, B. Bursten, S.-M. Peng and V.L. Goedken, *J. Am. Chem. Soc., 98* (1976) 8021.
[9] V.L. Goedken, S.-M. Peng, J. Molin-Norris and Y. Park, *J. Am. Chem. Soc., 98* (1976) 8391.
[10] P.J. Hochgesang and R.D. Bereman, *Inorg. Chim. Acta, 156* (1989) 213.
[11] P.J. Hochgesang and R.D. Bereman, *Inorg. Chim. Acta, 162* (1989) 191.
[12] P.J. Hochgesang and R.D. Bereman, *Inorg. Chim. Acta, 167* (1990) 199.
[13] C.L. Bailey, R.D. Bereman, D.P. Rillema and R. Nowak, *Inorg. Chem., 25* (1986) 933.
[14] A. Deronzier and M.-J. Marques, *J. Electroanal. Chem., 265* (1989) 341.
[15] A. Deronzier and M.-J. Marques, *J. Electroanal. Chem., 334* (1992) 247.
[16] C.L. Bailey, R.D. Bereman, D.P. Rillema and R. Nowak, *Inorg. Chim. Acta, 116* (1986) L45.
[17] P.E. Ellis, Jr., and J.E. Lyons, *J. Chem. Soc., Chem. Commun.*, (1989) 1189.
[18] P.E. Ellis, Jr., and J.E. Lyons, *J. Chem. Soc., Chem. Commun.*, (1989) 1315.
[19] G.M. Brooke, J. Burdon and J.C. Tatlow, *J. Chem. Soc.*, (1961) 802.
[20] For example, see T. Nagai, G. Nishioka, M. Koyama, A. Ando, T. Miki and I. Kumadaki, *Chem. Pharm. Bull., 40* (1992) 593.
[21] R.W. Taft, Jr., in M.S. Newman (ed.), *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 556.
[22] J.A. MacPhee, A. Panaye and J.E. DuBois, *Tetrahedron, 34* (1978) 3553.
[23] N.L. Allinger, *J. Am. Chem. Soc., 99* (1977) 8127.
[24] P.J. Hochgesang and R.D. Bereman, *Inorg. Chim. Acta, 149* (1978) 69.