

at ~ 410 nm and extended absorption envelopes centered at ~ 660 nm. The electronic spectral properties of these polymers may be understood in terms of the band diagram, shown in Figure 3, derived by the n -way splitting of the monomeric $[ML_4(D_{4h})]$, HOMO (a_{1g}), and LUMO (a_{2u}) of a supposedly isolated linear chain section ($[ML_4]_n$ eclipsed) of the polymers.¹¹ Both the bonding (d_z) and antibonding ($p_z-\pi^*$) bands are comprised of n -filled ($2n$ electrons) and empty levels, respectively. The high-energy absorptions in the spectra of the polymers have been assigned as either top-to-top or bottom-to-bottom band transitions. These transitions should be similar in energy to the ${}^1A_{1g} \rightarrow {}^1A_{2u}$ transition in the monomer $Rh(CNPh)_4BPh_4$ (411 nm).⁵ The low-energy broad absorptions in the polymers have been assigned as a multitude of transitions occurring between the upper region of the bonding and the lower region of the antibonding bands. In view of their origin, these low-energy absorptions should be greatly affected by the breaking of intermetallic interactions in the polymers. Manifestation of this effect is found in the spectra of certain oxidized polymers such as those derived by the iodination (C) and photobleaching (D)¹² of polymer B (see Figure 2). Finally, we call attention to the overall ability of the new polymers A and B to extensively absorb light, especially in the visible region, which is illustrated in Figure 2 by comparison with the spectrum of TiO_2 , a known photoconductor.

The new coordination polymers reported herein, and others containing different transition elements and various rigid linkages, are currently under intensive investigation in our laboratory. These polymers are being developed in the context of unconventional materials having both fundamentally interesting and useful chemical and/or physical properties. Special emphasis in this program is placed on the study of new surfaces for catalysis and photocatalysis.

Acknowledgment. This research program was supported by generous funds received from KFA, NCRD, and Minerva.

(11) This approach represents an extension of the treatment proposed for oligomers by Gray et al.⁵ A somewhat similar band diagram was suggested by A. E. Underhill in "Low-Dimensional Cooperative Phenomena—The Possibility of High-Temperature Superconductivity", H. J. Keller, Ed., Plenum Press, New York and London, 1974, p 288.

(12) The yellow photobleached polymer D was obtained by irradiating the suspended polymer B in a 12 N HCl solution. The infrared spectra of the fully oxidized polymers (e.g., C and D) show one strong $\nu(NC)$ band at a frequency 40–50 cm^{-1} higher than those found in the starting polymers. Partially oxidized polymers, which can be obtained, for instance, by controlled halogenation, show $\nu(NC)$ bands in both $Rh(1+)$ and $Rh(3+)$ regions.

Avi Efraty,* Irene Feinstein, Felix Frolow, Lorenz Wackerle

Department of Organic Chemistry and
Department of Structural Chemistry
The Weizmann Institute of Science, Rehovot, Israel

Received March 25, 1980

Boron Analogues of the α -Amino Acids. Synthesis, X-ray Crystal Structure, and Biological Activity of Ammonia-Carboxyborane, the Boron Analogue of Glycine

Sir:

Glycine, $H_2NCH_2CO_2H$ or $H_3N^+CH_2CO_2^-$, may be considered the simplest α -amino acid and was the first to be discovered. We now report the synthesis and characterization of its isoelectronic and isosteric (protonated) boron analogue, ammonia-carboxyborane, $H_3N \cdot BH_2CO_2H$ (**1**), which may be viewed as the parent of a novel class of boron analogues of the common α -amino acids. Although we have previously reported the synthesis of other amine-carboxyboranes, e.g., $Me_3N \cdot BH_2CO_2H$, the boron analogue of betaine,¹ all previous examples did not contain hydrogen bonded

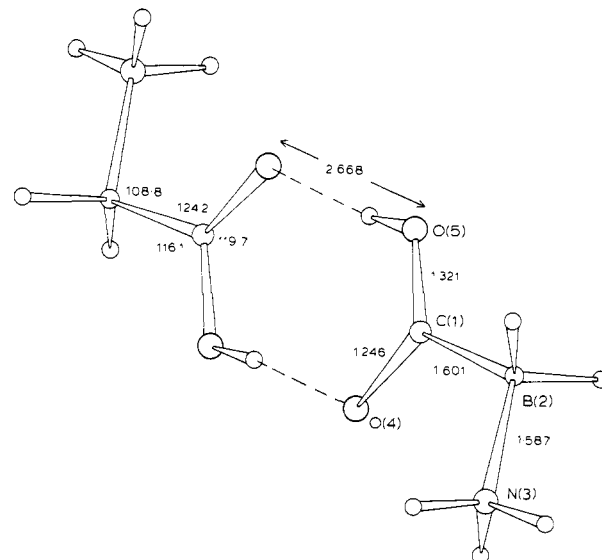


Figure 1. Conformation, interatomic distances (0.002–0.003 Å), and valency angles (0.2°) in the centrosymmetric $(H_3N \cdot BH_2CO_2H)_2$ dimer; small circles denote hydrogen atoms.

directly to nitrogen. An extremely important feature of the present example, like its glycine counterpart, is its potential to form peptide linkages and to be incorporated into proteins. The structure of **1** has been unequivocally established by single-crystal X-ray analysis, and its stability in several media has been investigated. Preliminary testing of **1** in animal model studies has demonstrated biological activity, in particular, significant antihyperlipidemic activity.

Preparation of **1** may be achieved by an amine exchange reaction. In a typical preparation, $Me_3N \cdot BH_2CO_2H$ was allowed to react with liquid NH_3 (ca. 1:10 w/w) in an evacuated stainless-steel cylinder at room temperature for 3 weeks after which time excess ammonia was allowed to evaporate off and removed finally by pumping out. The residue was transferred to a flask with the aid of dry $CHCl_3$, refluxed for 3–4 h, filtered hot, and washed with hot $CHCl_3$ to give $H_3N \cdot BH_2CO_2H$ as an insoluble residue. This procedure led to a yield of crude product in the 50–55% range which remained essentially constant even when the time of reaction was increased from 3 to 6 weeks; a reaction period of 2 weeks gives $H_3N \cdot BH_2CO_2H$ in 30% yield.² When the crude product is freshly crystallized from cold water, it melts at 116 °C, but this is lowered, with no observable change in spectral characteristics, after storage of the product in screw-capped vials over a period of time in normal laboratory conditions [IR (KBr in cm^{-1}) $\nu(NH)$, a broad envelope with peaks at 3330 (s), 3250 (s), 3200 (br, s); $\nu(OH)$ 3000 (br); $\nu(NH \cdots O)$ 2780 (br, s), 2650 (s); $\nu(BH)$ 2400 (s), 2340 (sh), 2250 (sh); $(\delta + \tau)$ (NH) 2050 (w), 1840 (br, w), 1760 (br, w); $\nu(CO)$ 1640 (s), $\delta(NH)$ 1605 (s)]. Anal. Calcd for $H_3N \cdot BH_2CO_2H$: C, 16.04; H, 8.02; N, 18.71; B, 14.44. Found: C, 15.83; H, 8.04; N, 18.53; B, 14.31.

Single-crystal X-ray analysis established the structure of **1** unequivocally. Monoclinic crystals of **1** belong to space group $P2_1/c$, with $a = 4.859$ (2), $b = 5.291$ (2), $c = 15.523$ (7) Å, $\beta = 108.42$ (3)°; $V = 378.6$ Å³; $Z = 4$; $d_{\text{calcd}} = 1.313$ g cm^{-3} . The structure was solved by direct methods with the MULTAN program package.³ Full-matrix least-squares refinement of atomic positional and thermal (anisotropic B, C, N, O; isotropic H) parameters converged to an R^4 value of 0.052 over 598 statistically significant [$I > 2.0\sigma(I)$] reflections measured on an Enraf-Nonius

(2) The Me_3N group in $Me_3N \cdot BH_2CN$ can also be replaced by NH_3 in a similar manner by reacting it with liquid NH_3 in a steel bomb to give about 20% yield of $H_3N \cdot BH_2CN$ in ca. 10 days. The unreacted $Me_3N \cdot BH_2CN$ can then be removed by sublimation, leaving $H_3N \cdot BH_2CN$ as a residue which may be purified by the usual procedures.

(3) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27A**, 368 (1971).

(4) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

(1) B. F. Spielvogel, L. Wojnowich, M. K. Das, A. T. McPhail, and K. D. Hargrave, *J. Am. Chem. Soc.*, **98**, 5703 (1976).

Table I. Comparison of Bond Lengths (Å) and Valency Angles (Deg) in $H_3N \cdot BH_2CO_2H$ and Some Structurally Related Compounds

	$CH_3YH_2C(O)O(H)$			
	$H_3N \cdot BH_2 \cdot CO_2H^a$	$NH_3CH_2 \cdot COOH^b$	$NH_3CH_2 \cdot COO^-^c$	$CH_3CH_2 \cdot COOH^d$
	lengths			
X-Y	1.587 (3)	1.481 (1)	1.475 (1)	1.536
Y-C	1.601 (3)	1.504 (1)	1.525 (1)	1.502
C=O	1.246 (2)	1.202 (1)	1.251 (1) ^e	1.226
C-O	1.321 (2)	1.312 (1)	1.251 (1) ^e	1.324
O-H...O	2.668 (2)			2.644
	angles			
X-Y-C	108.8 (2)	110.3 (1)	111.8 (1)	113.0
Y-C=O	124.2 (2)	123.4 (1)	117.4 (1) ^e	124.0
Y-C-O	116.1 (2)	111.6 (1)	117.4 (1) ^e	113.7
O=C-O	119.7 (2)	125.0 (1)	125.5 (1)	122.2

^a Present work. ^b Glycine hydrochloride, neutron diffraction: A. R. Al-Karaghoul, M. S. Lehmann, C. F. Miskell, J. J. Verbist, and T. F. Koetzle, *J. Chem. Phys.*, **63**, 1360 (1975). ^c α -Glycine, neutron diffraction: L. F. Power, K. E. Turner, and F. H. Moore, *Acta Crystallogr., Sect. B*, **32B**, 11 (1976). ^d F. S. Strieter, D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Crystallogr.*, **15**, 1233 (1962). ^e Equal, owing to the presence of the $-COO^-$ group.

CAD-3 automated diffractometer (Ni-filtered $Cu K\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$; θ - 2θ scans). Although molecules of **1** exist in the solid state in a form typical of optically inactive or racemic carboxylic acids, i.e., as centrosymmetric dimers (see Figure 1), they have a slightly longer, and thus weaker, O-H...O hydrogen-bonded distance [$O \cdots O = 2.668(2) \text{ \AA}$ in **1** vs. ca. 2.64 \AA in simple acids⁵]. Dimers of **1** are further associated via interdimer N-H...O hydrogen bonds ($N \cdots O = 2.981$ and 3.157 \AA) involving two of the amino hydrogen atoms, a class of relatively strong intermolecular interactions not available to simple carboxylic acids, and a feature which must be partly responsible for the elevated melting point of **1** compared to propionic acid ($-20.8 \text{ }^\circ\text{C}$). Bond lengths and valency angles for **1** are presented in Table I along with corresponding values for glycine, glycine hydrochloride, and propionic acid. Comparison of the valency angles at the carboxy groups reveals a significantly smaller difference between the B-C-O and O=C-O angles in **1** ($\Delta 3.6^\circ$) and those in glycine hydrochloride ($\Delta 13.4^\circ$) and propionic acid ($\Delta 8.5^\circ$). In addition, the N-B-C angle in **1** is smaller than that of $114.4(10)^\circ$ in $Me_3N \cdot BH_2CO_2H$, presumably as a consequence of reduced steric factors in **1**.

Hydrolysis of **1** occurs very slowly as manifested by the observation that a 0.118 M solution of **1** in water underwent only trace decomposition in 3 h. Very slow decomposition of **1** also took place in alkali; e.g., a 0.126 M solution of **1** in 1 N NaOH underwent only 0.33% decomposition in 3 h, with tapering off after that time, only trace amounts of gas being evolved in the following 3 days. In contrast, **1** is readily hydrolyzed in acid; e.g., a 2.23:1 mole ratio of gas to **1** was evolved after 3.5 h from a 0.126 M solution of **1** in 1 N HCl , and this increased to 2.27 after 20.5 h, by which time gas evolution was complete. A total of 2 mol of H_2 per mol of **1** would be anticipated, assuming that only hydrolysis of the B-H bonds occurs. However, IR analysis of the evolved gas showed that it contained CO, a fact which may be indicative of the involvement of a carbonyl intermediate, $[H_3N \cdot BH_2CO]^+$, which could undergo subsequent hydrolysis to yield CO and H_2 . That compound **1** is reasonably thermally stable was demonstrated by heating 0.778 mmol of **1** in an evacuated flask at $60 \text{ }^\circ\text{C}$ for 8 h when only 0.55 mol % was found to be decomposed.

(5) I. Nahringer, *Acta Chem. Scand.*, **24**, 453 (1970); F. J. Strieter, D. H. Templeton, R. F. Scheuerman, and R. L. Sass, *Acta Crystallogr.*, **15**, 1233 (1962); F. J. Strieter and D. H. Templeton, *ibid.*, **15**, 1240 (1962); R. F. Scheuerman and R. L. Sass, *ibid.*, **15**, 1244 (1962).

(6) A like difference ($\Delta 5.6^\circ$) was found in $Me_3N \cdot BH_2CO_2H$.

Significant antitumor⁷ and antihyperlipidemic⁸ activities were found when dosages of 20 mg/kg per day of **1** were administered to CF_1 male mice; the LD_{50} ⁹ is $>0.2 \text{ g/kg}$. In the Ehrlich ascites screen, inhibition of tumor growth was 76.5% for **1**, while lowering of the serum cholesterol level was 44% after 9 days and 60% after 16 days.

Acknowledgment. This research was supported in part by the Army Research Office. M.K.D. thanks the authorities of Jadavpur University, India, for a leave of absence.

(7) According to standard procedures, see: C. Piantadosi, C. S. Kim, and J. L. Irwin, *J. Pharm. Sci.*, **58**, 821 (1969). The control in this screen, 6-mercaptopurine, showed 99% inhibition.

(8) Serum cholesterol was assayed by means of the Lieberman-Burchard reaction. The control in this assay, clofibrate, which requires 300 mg/kg for significant antihyperlipidemic activity, showed 98% inhibition.

(9) The LD_{50} value was determined by use of the method of J. T. Litchfield and F. Wilcoxon, *J. Pharmacol. Exp. Ther.*, **96**, 99 (1949).

**Bernard F. Spielvogel,* Mrinal K. Das, Andrew T. McPhail*
Kay D. Onan**

*Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706*

Iris H. Hall*

*Division of Medicinal Chemistry, School of Pharmacy
University of North Carolina, Chapel Hill
Chapel Hill, North Carolina 27514*

Received December 10, 1979

Synthesis, Structure, and Equilibration of *s*-Cis- and *s*-Trans- η^4 -conjugated Diene-Zirconocene Complexes

Sir:

For numerous cases, it has been demonstrated that acyclic conjugated dienes when η^4 bound to a transition-metal center favor the *s*-cis arrangement over the *s*-trans geometry,¹ independent of the preferred conformation adopted by the free ligand.² We have for the first time obtained conclusive evidence that a conjugated diene can bind very well to a single metal atom through both double bonds and still in principle retain its favored transoid geometry. We report several examples of η^4 -diene-zirconocene complexes where the '*s*-trans isomer' has been found equal (or even higher) in thermodynamic stability to the corresponding '*s*-cis' form, depending on the substitution of the polyolefin.

We recently observed that photochemical activation of di-arylzirconocene complexes yields biaryls formed strictly by intramolecular coupling.³ This photoreaction can be very efficiently used to generate and transfer the elusive bis(η^5 -cyclopentadienyl)zirconium(II) to a variety of substrates. If the photolysis of diphenylzirconocene (2% in toluene, $-30 \text{ }^\circ\text{C}$, HPK 125, Pyrex filter) is carried out in the presence of suitable conjugated dienes (10% excess), the corresponding monomeric η^4 -diene-zirconocene complexes are formed.⁴ After workup at ambient temperature and fractional crystallization from toluene, we isolated $Cp_2Zr(\eta^4\text{-diene})$ complexes [diene = 1,3-butadiene (**1**, **1a**), isoprene (**2**), 2,3-dimethylbutadiene (**3**), *trans,trans*-

(1) Systems showing an *s*-trans-conjugated diene bridging a metal-metal bond have been reported: Sasse, H. E.; Ziegler, M. L. *Z. Anorg. Allg. Chem.* **1972**, **392**, 167-172. Pierpont, C. G. *Inorg. Chem.* **1978**, **17**, 1976-1980. (2) Tai, C. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, **98**, 7928-7932. Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet, F. A. L. *Ibid.* **1979**, **101**, 3657-3659.

(3) Erker, G. *J. Organomet. Chem.* **1977**, **134**, 189-202. See also: Rausch, M. D.; Boon, W. H.; Alt, H. G. *Ibid.* **1977**, **141**, 299-312. Rausch, M. D.; Boon, W. H.; Mintz, E. A. *Ibid.* **1978**, **160**, 81-92.

(4) Instead of the formation of isolable complexes, with some substrates catalytic isomerizations and hydrogen-transfer reactions occur; e.g., benzene and cyclooctene are obtained from a 1:1 mixture of any of the cyclohexadiene plus cyclooctadiene isomers.