placement when **8** is treated with strong bases. Thus, methyllithium and **8** gave bis(1-methylborabenzene)iron in 87% yield. Similarly, the reaction of **8** with $LiAlH_4$ gave 85% of the desired **4**. Bis(borabenzene)iron, obtained as red octahedral crystals which sublimed at 165 °C, is readily characterized by its mass spectra *m/e* 210 (base peak, M^+ for $C_{10}H_{12}{}^{11}B_2{}^{56}Fe$), ^{11}B NMR δ 13.6 (d, J_{BH} = 129.4 Hz), and Ir (KBr) 2510 cm^{-1} (BH). The ^1H NMR spectrum shows a very closely spaced pattern consisting of a six-proton multiplet centered at δ 4.87 ($H_{3,5}$, H_4) and a four-proton multiplet at δ 4.63 ($H_{2,6}$). The ^{11}B decoupled proton spectrum showed the B–H resonance also at δ 4.63.

Crystals of **4** grown from toluene–heptane were subjected to a preliminary X-ray diffraction study. They belonged to the cubic crystal class, with a cell constant a = 9.799 Å. The data were consistent with space group P_a3. Since the measured density of 1.47 g/cm³ (calcd 1.48 g/cm³) requires four molecules of $C_{10}H_{12}B_2Fe$ in the unit cell, the molecules must lie at special positions on threefold axes of the crystal. As the overall point symmetry of bis(borabenzene)iron can be no higher than C_{2h}, the boron and carbon atoms were not differentiated. Further refinement seemed unwarranted.[10] However, it is particularly interesting to note that bis(borabenzene)iron is isostructural with the isoelectronic bis(benzene)chromium.[11]

Attempts to metalate bis(borabenzene)iron with butyllithium (ferrocene metalation conditions) gave only hydride displacement to bis(1-butylborabenzene)iron. Although **4** is ultimately destroyed by treatment with trifluoroacetic acid-*d*, the reisolated bis(borabenzene)iron shows incorporation of up to four α-D atoms: mass spectral envelope *m/e* 214–210; ^1H NMR diminished intensity at δ 4.63. Exchange at BH was small since there was no strong B–D IR absorption.[12] Thus, bis(borabenzene)iron undergoes electrophilic aromatic substitution primarily at carbon (α) and nucleophilic substitution at boron.

Acknowledgment. This work was partially supported by grants from the National Science Foundation.

References and Notes

(1) Ashe, A. J., III; Shu, P. *J. Am. Chem. Soc.* **1971,** *93*, 1804. Sullivan, S. A.; Sandford, H., Beauchamp, J. L.; Ashe, A. J., III *Ibid.* **1978,** *100*, 3737.

(2) Herberich, G. E.; Greiss, G.; Heil, H. F. *Angew. Chem., Int. Ed. Engl.* **1970,** *9*, 805. Herberich, G. E.; Greiss, G. *Chem. Ber.* **1972,** *105*, 3413.

(3) Ashe, A. J., III; Meyers, E.; Shu, P.; Von Lehmann, T.; Bastide, J. *J. Am. Chem. Soc.* **1975,** *97*, 6865.

(4) Herberich, G. E.; Becker, H. J. *Angew. Chem., Int. Ed. Engl.* **1975,** *14*, 184. Herberich, G. E.; Becker, H. J.; Carsten, K.; Engelke, C.; Koch, W. *Chem. Ber.* **1976,** *109*, 2382.

(5) For a review see: Allen, C. W.; Palmer, D. E. *J. Chem. Educ.* **1978,** *55*, 497.

(6) However, INDO-SCF calculations are available for the parent system: Clack, D. W.; Warren, K. D. *Inorg. Chem.* **1979,** *18*, 513.

(7) All NMR spectra were recorded using a JEOL JNM•PS 100 FT spectrometer. Benzene-d_6 was the solvent in all cases.

(8) The ^1H NMR spectrum is rather similar to that reported for the analogous (cyclopentadienyl)(1-phenyl-1-bora-2,4-cyclohexadienyl)cobalt. Our assignment is made by analogy. Herberich, G. E.; Engelke, C.; Pahlmann, W. *Chem. Ber.* **1979,** *112*, 607.

(9) Herberich, G. E.; Müller, H. *Angew. Chem., Int. Ed. Engl.* **1971,** *10*, 937. Herberich, G. E.; Bauer, E.; Hengesbach, J.; Kölle, U.; Huttner, G.; Lorenz, H. *Chem. Ber.* **1977,** *110*, 760. Koelle, U.; Biersdorf, W.-D. H.; Herberich, G. E. *J. Organomet. Chem.* **1978,** *152*, 7.

(10) However, structures have been determined for several substituted borabenzene metal complexes. See: Huttner, G.; Krieg, B.; Gartzke, W. *Chem. Ber.* **1972,** *105*, 3424. Huttner, G.; Gartzke, W. *Ibid.* **1974,** *107*, 3786.

(11) Ibers, J. A. *J. Chem. Phys.* **1964,** *40*, 3129. $Cr(C_6H_6)_2$ has slightly smaller cell constant, a = 9.667 Å.

(12) Bis(borabenzene-d_1)iron, prepared from lithium aluminum deuteride and **8**, showed strong IR bands at 1920–1860 cm^{-1}. From the IR spectra of mixtures of bis(borabenzene)iron and bis(borabenzene-d_1)iron, it was estimated that there had been no more than 5% B–H exchange.

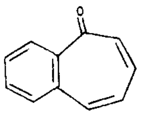
Arthur J. Ashe, III,* William Butler, Harold F. Sandford
Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109

Received June 18, 1979

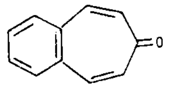
7-Phenoxy-3,4-benzotropone: Chemistry and Spectroscopy of an Isobenzotropone[1]

Sir:

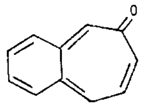
Semiempirical molecular orbital calculations predict strong stabilization by π-electron delocalization in 2,3-benzotropone (**1**, 20.6 kcal/mol) and 4,5-benzotropone (**2**, 18.7 kcal/mol).[2] In sharp contrast, these calculations predict that 3,4-benzotropone (**3**) will be only weakly stabilized (3.4 kcal/mol) by π-electron delocalization.[2] These calculations also suggest that the tropone moiety has a bond-alternate structure and contributes little to the π-electron stabilization.[2] Examples of **1** and **2** have been known for some time.[3] Information on systems related to **3** is almost completely lacking. Bauld has provided chemical trapping evidence for ortho quinoidal dibenzotropones and has reported ν_{CO} values for these intriguing molecules,[4] and Yoshioka et al.[5] have suggested 2-hydroxy-3,4-benzotropone as an intermediate in a reaction. We report the generation and chemical and spectroscopic characterization of 7-phenoxy-3,4-benzotropone, an isobenzotropone.



1

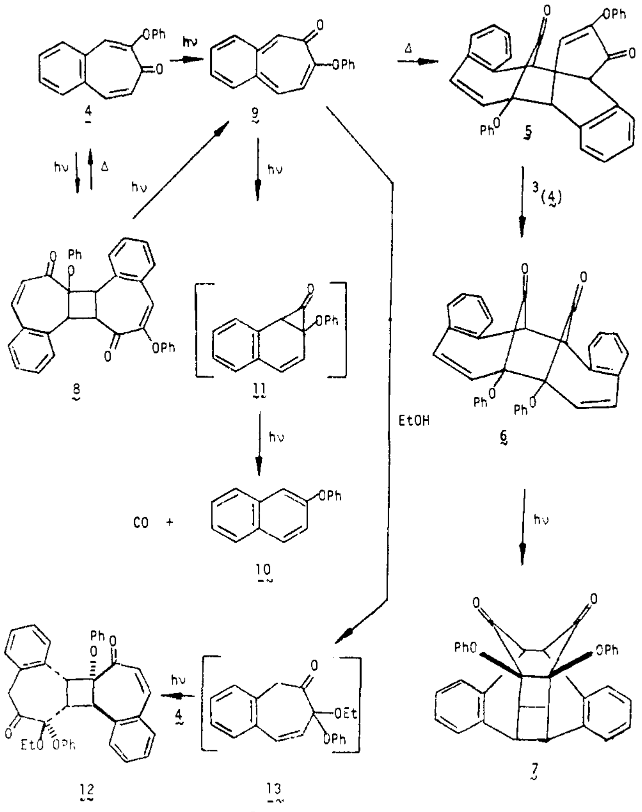


2



3

We have shown previously that irradiation of 2-phenoxy-4,5-benzotropone (**4**) gives three rearranged dimers (**5–7**).[6]



Labeling studies with ^{18}O labels in either the carbonyl group or the phenoxy group show that an oxygen to oxygen phenyl shift occurs in the formation of the dimers.[7] Irradiation of **4** in ethanol at −75 °C or at concentrations $>10^{-2}$ M in ethanol at room temperature gives a new dimer (**8**)[8] in addition to **5** and **6**.

Irradiation (<400 nm) of **4** in dilute ethanol solution at −78 °C produces a photostationary state involving **4** and a new product identified as 7-phenoxy-3,4-benzotropone (**9**), by the observations which follow. Irradiation (>400 nm) of the new product regenerates **4**. The ultraviolet spectrum of **9** shows

0002-7863/79/1501-7067$01.00/0

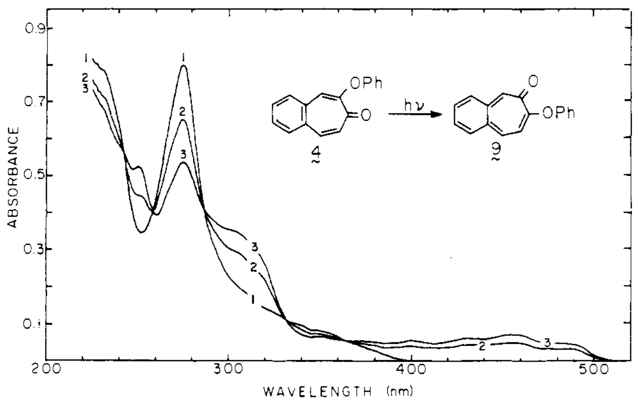


Figure 1. UV-visible absorption spectrum from photoconversion of 3.41 × 10^{-6} M 2-phenoxy-4,5-benzotropone (**4**) to 7-phenoxy-3,4-benzotropone (**9**) in ethanol under argon at −78 °C.: (1) prior to irradiation, (2) irradiation for 6 s through a Corning CS7-54 band-pass filter (228-420 nm), (3) irradiation for 6 s more.

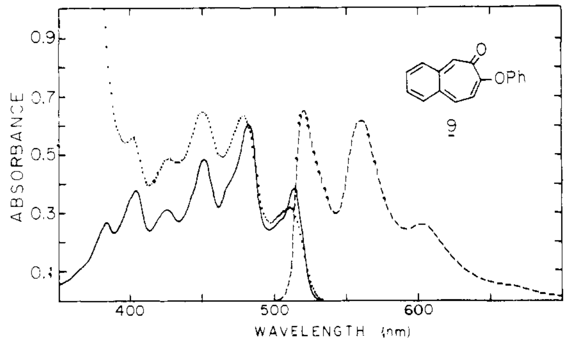


Figure 2. Uncorrected fluorescence emission (- - -), excitation (—), and absorption (···) spectra of 7-phenoxy-3,4-benzotropone (**9**) in 2-methyltetrahydrofuran at 77 K.

maxima at 251, 268 (sh), 276, 301, 314 (sh), 378, 401, 435, 458, and 483 nm and several isosbestic points (Figure 1). The molar extinction coefficient at 458 nm is ~5000.[10] Compound **9** shows strong, structured fluorescence in the visible region λ_{max} (2-MeTHF) 520, 560, and 603 nm. The emission spectrum is independent of excitation wavelength, and the excitation spectrum is independent of the monitoring wavelength. The onset of the absorption and emission spectra overlap (Figure 2). The fluorescence lifetime in ethanol at 77 K is 19.8 ns.[11] The emission intensity depends strongly on temperature and solvent. The relative intensities at 273, 200, and 77 K are 1:10^2:10^4. The intensity in 25% methanol-water is ~10^2 times that in ethanol or 2-methyltetrahydrofuran. The absorption and emission spectra of **9** are quite similar to those of *o*-xylylene,[12] substituted *o*-xylylenes,[13] and heteronuclear bicyclic *o*-xylylenes.[14]

Irradiation (<400 nm) of **4** matrix isolated in argon at 26 K also generates **9** which has infrared bands at 1615-1625, 1575, 1650, 1470, 1250, and 1180 cm^{-1}. Irradiation (>400 nm) of **9** in argon regenerates **4** at a rate far slower than that observed at −78 °C. Prolonged irradiation (<400 nm) destroys both **4** and **9** giving carbon monoxide (2110 cm^{-1}). The other major product from the reaction was identified after isolation as β-phenoxynaphthalene (**10**) (LC retention time and UV spectrum). The loss of carbon monoxide probably proceeds via the cyclopropanone derivative **11**. A similar loss of carbon monoxide is observed in the mass spectrum of **4**[15]

When ethanol solutions of **9** are warmed to room temperature, the product is dimer **5**. The disappearance of **9** monitored at 458 *nm* follows second-order kinetics. Rate constants for the disappearance of **9** in ethanol at 297.3, 283.2, 272.2, and 255.4 K are 7.54, 3.99, 2.63, and 1.08 M^{-1} s^{-1}, respectively. Below

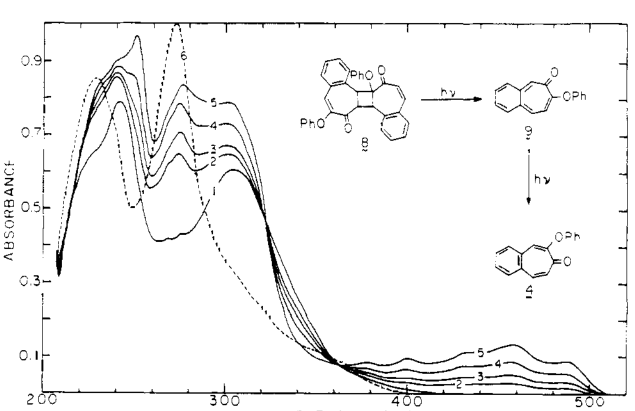
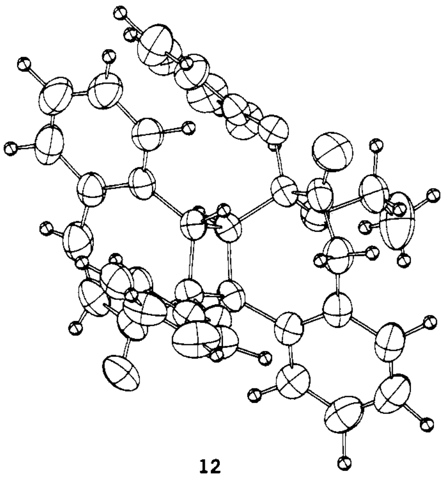


Figure 3. UV-visible spectrum from photoconversion of 8.00 × 10^{-6} M **8** to 7-phenoxy-3,4-benzotropone (**9**) and **9** to **4** in ethanol at −78 °C: (1) prior to irradiation, (2) irradiation for 18 s through a Corning CS7-54 band-pass filter (288-420 nm), (3) irradiation for 12 s more, (4) irradiation for 30 s more, (5) irradiation for 90 s more, (6) irradiation for 5 min with λ >418 nm.

−50 °C, **9** is stable indefinitely. The activation parameters at 298.15 K are $\Delta H^{\ddagger}$ = 5.9 kcal/mol and $\Delta S^{\ddagger}$ = −31.7 cal mol^{-1} deg^{-1}. The large negative entropy of activation strongly suggests that the dimerization process is the thermally allowed $[_{\pi}8_s + _{\pi}10_s]$ cycloaddition.

Trapping of 7-phenoxy-3,4-benzotropone has been achieved in the isolation of a crystalline minor product (**12**). The process in which **12** is formed involves photocycloaddition of **4** to the ethanol adduct **13** of **9**. Structure **12** was established by X-ray crystallography, with a clear crystal, ~0.4 × 0.4 × 0.3 mm, grown from a mixture of chloroform and hexane. Data were collected at 23 °C on a Syntex P$\bar{1}$ automated diffractometer with monochromatized Mo Kα radiation (0.7107 Å). The space group was $P2_1/n$, with cell dimensions a = 15.937 (4), b = 11.875 (3), c = 17.169 (3) Å and β = 96.39 (2)°. The density calculated for Z = 4, including one molecule of $CHCl_3$ in the asymmetric unit, is 1.364 g mL^{-1}; the density measured by flotation is 1.342 g mL^{-1}, corresponding to an occupancy of 0.92 for the $CHCl_3$. Out of 6069 unique reflections with 2θ ≤ 51°, 3861 with $I \geq 1.5\sigma(I)$ were used in the structure determination and refinement. The structure was readily solved with MULTAN,[16] 36 of the 41 C and O atoms of the molecule and the three Cl atoms being found at once, and the six remaining C and O atoms appearing in a difference map. Refinement by full-matrix least squares with anisotropic vibration parameters and a subsequent difference map that revealed all 31 H atoms in the asymmetric unit led eventually to R = 0.076 (R_w = 0.074); the average esd of a C-C bond length is ~0.007 Å. The structural details will be published elsewhere.



12

Irradiation (<400 nm) of dimer **8** also gives **9**. This surprising transformation uses only one quantum of light and does not involve intermediates. Isosbestic points at 324 and 363 nm are clearly observed (Figure 3).

The thermal chemistry of 7-phenoxy-3,4-benzotropone (**9**) clarifies the formation of dimer **5**. Dimer **6** appears to be a primary product under certain conditions[17] but can also be formed from the triplet state of dimer **5**. Energy transfer from triplet 2-phenoxy-4,5-benzotropone to **5** has been shown to produce **6**. Oxygen quenches the formation of **6** and **8**. Dimer **7** is formed on direct irradiation of **6** and is clearly not a primary product.[6]

Acknowledgment. This research was supported by Grant GM 24427 from the National Institutes of General Medical Sciences, U.S. Public Health Service, Department of Health, Education, and Welfare. The X-ray diffractometer was provided to the Department of Chemistry by NSF Grant GP 28248 and the fluorescence spectrometer by NSF Grant MPS75-06135. The authors thank Professor Malcom Nicol and Dr. Mary Anton for the fluorescence lifetime measurement.

References and Notes

(1) Presented in part at the 176th National Meeting of the American Chemical Society, April 1978, Anaheim, Calif.

(2) M. J. S. Dewar and N. Trinajstic, *Croat. Chem. Acta*, **42**, 1–12 (1970); N. Trinajstic, *Rec. Chem. Prog.*, **32**, 85–97 (1971).

(3) T. Nozoe, "Non-benzenoid Hydrocarbons", D. Ginsburg, Ed., Interscience, New York, 1959, pp 339–463.

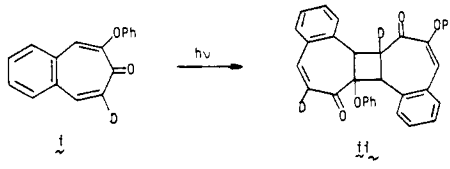
(4) N. L. Bauld and Y. S. Rim, *J. Am. Chem. Soc.*, **89**, 178–179 (1967); C. E. Hudson and N. L. Bauld, *ibid.*, **95**, 3822–3823 (1973).

(5) M. Yoshioka, I. Saito, H. Hoshino, and S. Ebine, *J. Chem. Soc. D*, 782 (1970).

(6) O. L. Chapman, H. G. Smith, R. W. King, D. J. Pasto, and M. R. Stoner, *J. Am. Chem. Soc.*, **85**, 2031–2032 (1963).

(7) M.-T. Sung, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1967.

(8) Dimer **8** on heating to 210 °C gives **4** in quantitative yield. The mass spectrum of **8** shows a parent ion at *m/e* 496 and the base peak at *m/e* 248. The infrared spectrum of **8** shows an intense band at 1670 cm^{-1} (ν_{CO}), and the ultraviolet spectrum has λ_{max}^{EtOH} 208 (48 000), 234 (24 000), 266 (sh, 9600), 276 (9600), and 305 nm (15 000). The ^{1}H NMR spectrum ($CHCl_3$, δ) shows a broad multiplet at 6.96–7.47 (13 H aromatic plus 1 H olefinic), a multiplet at 6.84 (2 H, phenolic meta protons), a multiplet at 6.76 (1 H, phenolic para proton), a multiplet at 6.22 (2 H, phenolic ortho protons), an AX pattern at 7.31 and 6.54 (J_{AX} = 12.6 Hz), and an AMX pattern at 4.59, 4.37, and 3.97 (J_{AX} = 11.0, J_{MX} = 9.5, $J_{AM} \simeq$ 0 Hz). The low-field portion of the AX system was observed directly by difference decoupling techniques. When 7-deuterio-2-phenoxy-3,4-benzotropone (i) is irradiated, dideuterio dimer **8** (ii) is formed. The NMR spectrum of ii has, in addition



to the aromatic protons and the low-field olefinic protons, only two singlets at δ 4.59 and 4.37. The stereochemistry of dimer **8** has not been determined.

(9) The reason that the intermediate **9** was not observed in previous studies is the much greater quantum yield for the reverse process and the visible light absorption by **9**.

(10) The molar extinction coefficient of **9** at 458 nm in ethanol was calculated from the optical density and molar extinction coefficient (43 400) at 273 nm of **4** formed from irradiation with λ >420 nm of **9** which had been formed from very high photoconversion of **8** (see Figure 3).

(11) This measurement was made by Dr. Mary Anton and Professor Malcolm Nicol.

(12) C. R. Flynn and J. Michl, *J. Am. Chem. Soc.*, **95**, 5802–5083 (1973); **96**, 3280–3288 (1974). K. L. Tseung and J. Michl, *ibid.*, **99**, 4840–4842 (1977). E. Migirdicyan and J. Bandet, *ibid.*, **97**, 7400–7404 (1975).

(13) R. D. Miller, J. Kolc, and J. Michl, *J. Am. Chem. Soc.*, **98**, 8510–8514 (1976); W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horak, *ibid.*, **99**, 3876–3877 (1977); D. S. Matteson and R. A. Davis, *J. Chem. Soc. D*, 669–670 (1970).

(14) R. N. Warrener, *J. Am. Chem. Soc.*, **93**, 2346–2348 (1971); D. Wege, *Tetrahedron Lett.*, 2337–2338 (1971); R. Bonnett and R. F. C. Brown, *J. Chem. Soc. D*, 393–395 (1972); W. Rettig and J. Wirz, *Helv. Chim. Acta*, **59**, 1054–1074 (1976); J. M. Holland and D. W. Jones, *J. Chem. Soc. C*, 530–536, 536–540 (1970); D. W. Jones, *ibid.*, 1729–1732 (1969).

(15) T. H. Kinstle, O. L. Chapman, and M.-T. Sung, *J. Am. Chem. Soc.*, **90**, 1227–1234 (1968); **88**, 2618–2619 (1966).

(16) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368–376 (1971).

(17) Dimers **5** and **6** both appear to be primary products in the irradiation of neat 2-phenoxy-4,5-benzotropone at 77 K.

O. L. Chapman,* S. C. Busman, K. N. Trueblood
Department of Chemistry
University of California, Los Angeles
Los Angeles, California 90024

Received May 21, 1979

Investigation of the System CO_2–HCO_3^- in the Presence of Copper(II) Bovine Carbonic Anhydrase B

Sir:

The hydration of CO_2 and dehydration of HCO_3^- are catalyzed by carbonic anhydrase isoenzymes and by the cobalt-substituted derivatives at a rate which can be very high.[1-6] One of the major problems in understanding the catalytic mechanism is to identify the binding sites of both HCO_3^- and CO_2 within the active site cavity.[2,7,8] ^{13}C NMR studies on the native enzyme–substrate and cobalt derivative–substrate systems have been performed. The high activity forms (bovine and human C) are capable of causing coalescence of the two signals of the CO_2 and HCO_3^- species.[9] If added in limited amounts the enzyme causes line broadening of the two signals, whose analysis may provide useful kinetic information.[10,11] In the case of the cobalt-substituted low-activity human carbonic anhydrase B the $CO_2 \rightleftharpoons HCO_3^-$ interconversion frequency is lower than the difference in chemical shift, whereas it is higher than the experimental T_1^{-1} values.[12] Therefore two separate signals were observed for CO_2 and HCO_3^-, but the T_1^{-1} values were the same for the two signals. The T_1^{-1} values, however, were substantially independent of pH, thus indicating that the average C–Co distance is constant, and typical of short-range interactions. Therefore the possibility that CO_2 is directly bound at the metal was taken into consideration.[12] On the other hand coordination of CO_2 to metals in inorganic models is quite rare. So far, CO_2 as such has been found to bind transition metals only through carbon,[13] or through both carbon and oxygen.[14] To better characterize the type of interactions between the two interconverting species, CO_2 and HCO_3^-, with metals in carbonic anhydrase derivatives, the copper-substituted bovine carbonic anhydrase B (CuBCAB) has been investigated. The choice of this metal ion is based on its high relaxing capability compared to cobalt[15-17] and on the very low catalytic activity of its enzyme derivative.[18] The latter property allows longer independent life of the two substrate species, whereas, owing to shorter ^{13}C relaxation times, a shorter lifetime is enough to provide information on the interaction of a single substrate species with the surroundings. Therefore the NMR parameters of the ^{13}C nuclei will result from independent interaction of each single species with the paramagnetic center rather than by the average due to the interconversion. Furthermore copper(II) has a large affinity for ligands[19] and, indeed, copper carbonic anhydrase shows a larger affinity for inhibitors than any other metallo-substituted carbonic anhydrase.[20]

Bovine carbonic anhydrase B obtained through chromatography[21] of the commercial enzyme (Sigma) was carefully demetallized[6] to a zinc content of <5% as monitored by esterase activity[22] and then reacted with copper sulfate.[16] Since relatively low concentrations of native enzyme could considerably shorten the lifetimes of the CO_2 and HCO_3^- species, thus averaging their relaxation rates, 10% of acetazolamide with respect to the total amount of enzyme was always added to the copper carbonic anhydrase solutions. The affinity constant of the above inhibitor for the zinc enzyme ($\sim 10^7$ M^{-1})