Since the carbon–carbon double bond in cyclopropene has a length of 1.304 (3) Å[14] and the boron–carbon bond in trivinylborane has a length of 1.558 Å,[14] it is evident that the carbon–carbon bond in **2** has been lengthened by 0.11 Å and the boron–carbon bond contracted by 0.14 Å. Therefore, these bond length changes strongly support the conclusion that the two π-electrons in the borirene ring are completely delocalized among the boron and carbon p-orbitals. Thus the ring can be viewed as having Hückel aromaticity, quite analogous to that of the triphenylcyclopropenium cation.[15,16]

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Supplementary Material Available: Tables of atom coordinates, bond distances and angles, and anisotropic thermal parameters (3 pages); listing of observed vs. calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(16) While one might consider that the disorder in the BC_2 ring would cast doubt on the claim of equality of the bond distances in the three-membered ring, the presence of an approximately equilateral array for the BC_2 atoms is supported by the nearly equivalent arrangement of the three mesityl rings. It is true that the crystallographic site symmetry could have accommodated an isosceles BC_2 array with a 0.26-Å difference in the B–C and C–C bond distances. However, if the bond distances were so different, the mesityl rings would have chosen some other torsional arrangement: the adjacent mesityl groups on the supposed C=C bond would be expected to be twisted with their ring planes more toward the perpendicular to the plane defined by the BC_2 array than would be the mesityl appended to boron. That the three mesityl groups have the same torsional angle with respect to the BC_2 plane means that the difference in the actual separations, C–C and B–C, cannot be anywhere nearly as large as such hypothetical, localized bonding description would require. It should be noted that ab initio molecular orbital calculations utilizing modified versions of GAUSSIAN 70 and GAUSSIAN 76 series of programs have been carried out on borirene, BC_2H_3, by using split valence 4-31G basis and estimating correlation energies through application of Møller–Plesset second-order perturbation theory at the 4-31G basis set level. The calculated B–C bond length is 1.476 Å, and the C–C bond distance 1.347 Å. These calculations are at variance with our experimental findings. Cf.: Krogh-Jespersen, K.; Cremer, D.; Dill, J. D.; Pople, J. A.; Schleyer, P. v. R. *J. Am Chem. Soc.* **1981**, *103*, 2589.

High-Temperature Superconductivity in Y-Ba-Cu-O: Identification of a Copper-Rich Superconducting Phase

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For the past 15 years, advances in superconductivity have come about only slowly and even a 0.5 K increase in transition temperature was noteworthy. Until April 1986, the highest transition temperatures were near 23 K. At that time, Bednorz and Müller reported superconductivity in La–Ba–Cu–O compounds above 30 K.[1] Following this breakthrough, there were further studies of these phases and superconductivity was found also in similar solids containing Sr and Ca instead of Ba.[2-7] The superconducting phase was identified as a layered perovskite $A_{2-x}B_xCuO_4$ with tetragonal symmetry, where A = La^{3+} and B = Ca^{2+}, Sr^{2+}, or Ba^{2+}. The Sr compounds with $x = 0.15$ show the highest transition temperatures with T_c near 36 K.[5] These studies lead to the investigation of other ternary copper oxides and soon thereafter Chu and co-workers[8,9] found that compounds with a nominal composition of $Y_{1.2}Ba_{0.8}CuO_4$ could be prepared with superconducting transitions near 100 K. In contrast to the $La_{2-x}Sr_xCuO_4$ phases, the analogous $Y_{2-x}Ba_xCuO_4$ materials contain more than one phase. We report here the composition and properties of a superconducting phase containing Y, Ba, Cu, and O which is copper-rich compared with $Y_{1.2}Ba_{0.8}CuO_4$.

Chu and co-workers[8,9] and a number of other investigators[10-12] began to study $Y_{2-x}Ba_xCuO_4$ phases; our work[10] was motivated by the hope that the superconducting properties of $La_{2-x}Ba_xCuO_4$ could be tailored by substituting the smaller cation Y^{3+} for La^{3+}. It was almost beyond dreams to discover that some samples of nominal composition $Y_{2-x}Ba_xCuO_4$ superconducted above liquid nitrogen temperatures. However, it was evident from magnetic studies that only a small portion of the sample was superconducting and X-ray powder diffraction patterns indicated that no layered perovskite phases were present in the materials. The superconducting samples with nominal composition $Y_{1.2}Ba_{0.8}CuO_4$ are composed of at least two Y–Ba–Cu–O phases of different stoichiometries; a green phase and a black phase are easily distinguished under a light microscope. Unfortunately, due to the small crystallite size and extensive intergrowth, it has not been possible to separate the phases for analysis. In order to understand the chemistry of these materials, we synthesized and characterized $Y_{1-x}Ba_xCu_yO_z$ materials with various stoichiometries and have bracketed the stoichiometry of the superconducting phase.

Samples of nominal composition $Y_{1-x}Ba_xCu_yO_z$ with $0.15 < x < 0.55$ and $0.25 < y < 2$ were prepared by reacting stoichiometric ratios of Y_2O_3 (Alpha Products), $BaCO_3$ (Fisher Scientific), and CuO (Fisher Scientific). Simply firing mixtures of the solids at elevated temperatures yielded materials with considerable intergrowth of phases. A more uniform material was obtained by starting with an intimate mixture of finely divided particles. This was achieved when the reactants where dissolved first in nitric acid and the solution was evaporated to dryness. The nitrates were decomposed at 800 °C for 2 h and the resulting grey powders were ground in a mortar, pressed into $^1/_4$-in. pellets at 8000 psi, and fired for 4 h at 1100 °C under a flow of oxygen in Pt crucibles. The samples were cooled to room temperature in 1 h. Powder X-ray diffraction patterns, scanning electron microscope images, and microprobe analyses were obtained for all the samples synthesized. The fraction of superconducting phase in the samples was determined by measuring the magnetization when the samples were cooled in a field of 12.5 G in a SQUID magnetometer, i.e., by measuring the Meissner effect.

Our initial experiments began with compositions near $x = 0.4$ and $y = 0.5$, since this is the nominal composition of the materials which had been reported to superconduct above liquid nitrogen temperature. The best samples contained only 2% of a superconducting phase as determined by the Meissner effect. The powder patterns were quite complex and showed at least two sets

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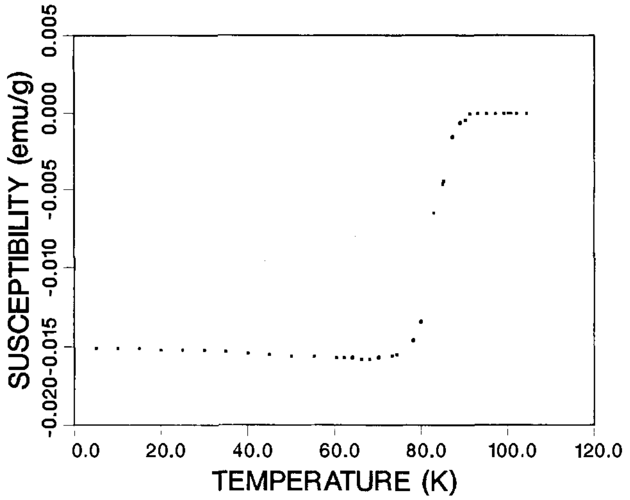

Figure 1. Gram susceptibility vs. temperature plot of $Y_{0.57}Ba_{0.43}Cu_{2.1}O_z$ measured in a field of 12.5 G. The onset of the superconducting state occurs at 90 K.

of lines whose intensity decreased or increased together as the composition was varied. Visually, the powders consisted mainly of a green phase with intergrowth of a black phase. Since the sample contained only a small portion of the superconducting phase and the green phase is an insulator, we postulate that the stoichiometry of the black phase is near that of the superconducting phase. Scanning electron microscope pictures of the samples showed bright particles adhering to dark particles, the dark being the major constituent. The dark particles corresponded to the green insulating phase and the bright particles to the black phase. Although microprobe analyses were difficult to obtain because the crystallites were small and the two phase so well mixed, the energy-dispersive X-ray spectra consistantly gave a Y:Ba ratio near the nominal composition. What varied across a given sample was the Y:Cu ratio. Analysis of the micrographs and the energy-dispersive X-ray spectra shows that the superconducting particles are copper-rich relative to the nominal Y:Cu stoichiometry. A Y:Cu ratio near 0.5:1 was common and this was assigned to the black phase. These results for the Y:Ba and Y:Cu ratios indicated that the superconducting phase has a stoichiometry near $x = 0.4$ and $y = 2$.

The magnetic properties of a sample with the nominal composition $Y_{0.57}Ba_{0.43}Cu_{2.1}O_z$ ($x = 0.43$ and $y = 2.1$) are shown in Figure 1. The measurements were made by using a SHE SQUID magnetometer in a field of 12.5 G; the field was calibrated by measuring the magnetization of a superconducting Sn sphere. Below 75 K, the magnetic susceptibility for our sample in a field of 12.5 G is −0.015 emu/g; this is ascribed to shielding. A rough measure of the density of the sample gave 5 g/cm^3 and therefore the volume susceptibility is −0.075 emu/cm^3. Since a superconductor is a perfect diamagnet,[13] the susceptibility should be $-1/4\pi$ emu/cm^3 = 0.08 emu/cm^3. Our sample shows approximately 100% shielding. The true Meissner effect, i.e., cooling the sample in a field, is roughly 10–20% of this value. Therefore, the sample contains 10–20% of the superconducting phase. The onset temperature T_0 is 90 K, the midpoint T_c is 85 K, and the transition width ΔT_c (10% to 90%) is 5 K.

Resistance measurements were made by using four probes attached to the sample with silver paint. A low-frequency ac technique was used with lock-in detection. The resistance of the sample was 65 mΩ at 87 K and dropped 3 orders of magnitude to 65 μΩ in less than 1 deg.

Table I. *d*-Spacings for a Sample with Nominal Composition $Y_{0.57}Ba_{0.43}Cu_{2.1}O_z$

2θ	d	I	phase
15.30	5.791	6	SC[a]
21.78	4.08	6	
22.85	3.892	30	SC
27.08	3.293	10	
27.93	3.194	5	SC
29.80	2.998	4	
30.47	2.934	16	
31.58	2.833	37	CuO
32.54	2.752	68	SC
32.84	2.727	100	SC
33.18	2.700	40	
33.61	2.666	15	
33.98	2.638	6	
35.54	2.526	65	CuO
36.50	2.462	4	SC
38.48	2.339	85	SC
38.69	2.327	75	Al
40.34	2.236	15	
44.72	2.026	60	Al
46.7	1.945	69	SC
47.75	1.905	12	SC
48.85	1.864	12	CuO
51.6	1.771	5	SC
51.97	1.760	7	
52.50	1.743	7	SC
53.6	1.710	7	SC
55.15	1.665	7	SC
55.7	1.650	5	
58.38	1.581	39	SC
58.95	1.567	16	SC
59.38	1.556	5	
60.9	1.521	7	
61.6	1.506	13	CuO
62.55	1.485	4	
65.87	1.418	9	CuO
66.35	1.409	8	CuO
68.2	1.375	20	CuO
68.9	1.363	14	SC

[a] SC = superconducting phase.

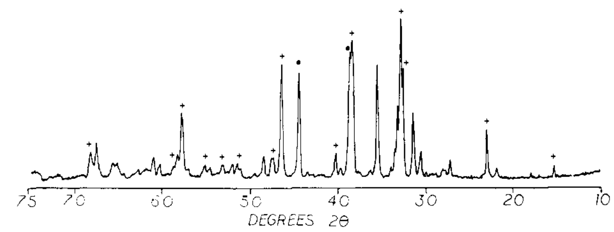

Figure 2. X-ray powder diffraction pattern of $Y_{0.57}Ba_{0.43}Cu_{2.1}O_z$. Lines arising from the aluminum sample holder are marked by (*) and the lines due to the superconducting phase are marked by (+).

The powder X-ray diffraction pattern of the sample is given in Figure 2 and the d-spacings are listed in Table I. We have identified the lines (+) in the X-ray pattern due to the superconducting phase by correlating intensities of various sets of lines in the X-ray patterns of samples of various compositions with the magnitude of the Meissner effect. Two lines (*) are due to the Al sample holder and the others arise from a Cu-poor phase (Y:Cu > 0.5) shown by our group to be nonsuperconducting or from excess CuO as indicated in Table I.

In summary, we have identified a superconducting phase that is more Cu-rich than other reported Y–Ba–Cu–O superconducting materials. This phase shows 10–20% Meissner effect, with $T_0 = 90$ K. Further, the most exciting aspect of this phase is that it is near a low melting (below 1200 °C) eutectic; if the phase melts congruently it will be possible to fashion wires. We are continuing efforts to fully characterize this superconducting phase including complete indexing of the X-ray powder pattern, as well as isolation of single crystals. Additional work to extend this study to related compositions is under way.

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ESR Study on the σ- and π-Radical Cations Formed by One-Electron Oxidation of Phenyldiazomethanes

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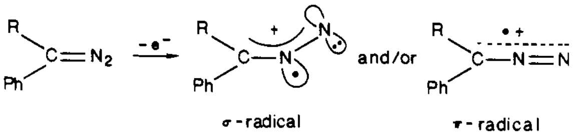
One-electron oxidations of diazomethanes have attracted much attention from mechanistic and synthetic standpoints.[1-4] The intermediacy of radical cations has often been suggested, but their direct observation could not be achieved spectroscopically[3] because of their short lifetimes as deduced from a voltammetric study.[4] Here, we report the first ESR study on the radical cations of phenyldiazomethanes in solution. Depending on substituents, the diazomethanes are shown to afford either σ- or π-radical cations of quite different electronic structures. The removal of one electron from the π-orbital (HOMO) of unhindered phenyldiazomethanes yields bent σ-radical cations by a turnover of the SOMO.

The ESR spectra of diazomethane radical cations were obtained during electrochemical oxidation[5] in a cavity at low temperature. When a degassed solution of diphenyldiazomethane (**1**) in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4 was electrolyzed at +1.3 V (vs. Ag/AgCl), a spectrum of $\mathbf{1}^{\bullet +}$ was observed (Figure 1a). The triplet of triplets pattern is due to the hyperfine coupling with two unequivalent nitrogens with large coupling constants, 1.72 and 1.01 mT.[6] When the electrolysis was stopped, this species decayed with half-lives of ~10 s at −33 °C and ~90 s at −83 °C. Similar spectra were observed for $(p\text{-}MeOC_6H_4)_2CN_2$ (**2**) and $Ph(Me)CN_2$ (**3**). Even when an α-methyl group is attached, couplings of protons were too small to resolve (Figure 1b). The coupling constants of two nitrogens are practically unchanged by substituents (Table I) and close to those (2.25 and 0.94 mT) of phenyldiazenyl, a reported σ-radical.[7] Thus, the radical cations of **1–3** seem to have a "σ-radical" structure, where an unpaired electron is localized on two nitrogens.



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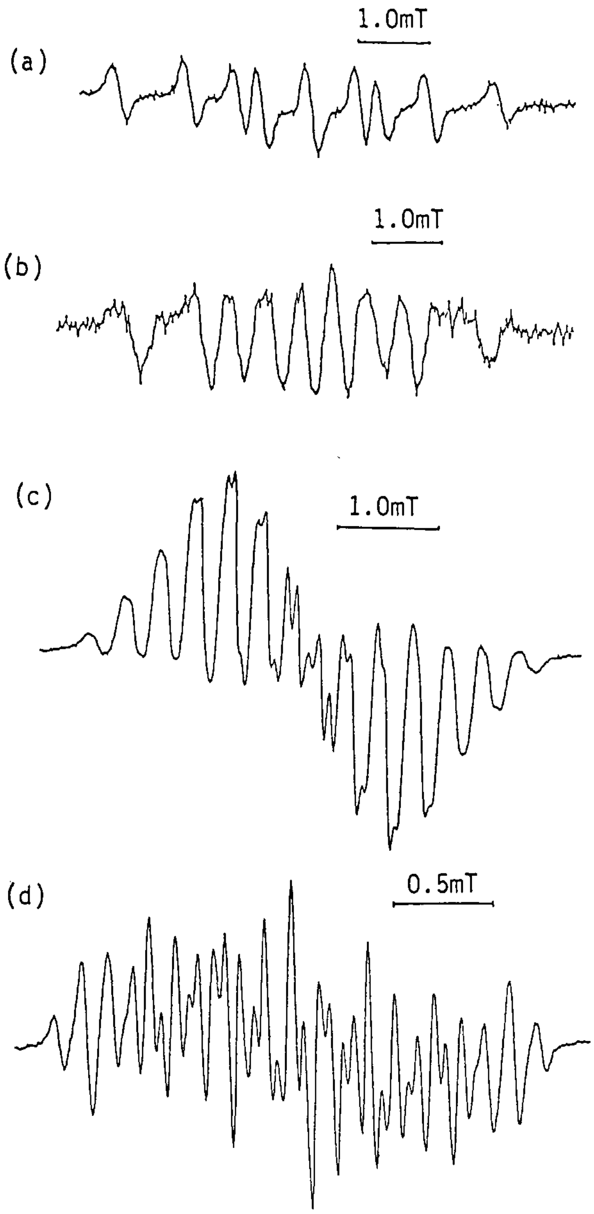

Figure 1. ESR spectra observed during the electrochemical oxidation of (a) **1** at −33 °C, (b) **3**, (c) **4**, and (d) **5** at −90 °C, in CH_2Cl_2 containing 0.1 M n-Bu_4NBF_4.

The one-electron removal from the π-orbital (HOMO) of phenyldiazomethanes[8] surely changes the resulting electronic configuration into a σ-radical structure. This interesting turnover is assumed to be due to a significant stabilizing interaction between phenyl and the resulting cation center. In order to reduce such an interaction, we studied diazomethanes with a *tert*-butyl substituent. In fact, a different type of ESR spectrum was observed in the case of $\mathbf{4}^{\bullet +}$ and $\mathbf{5}^{\bullet +}$ (Figure 1c and 1d). These radical cations were relatively stable with half-lives of ~10 and ~30 min, respectively, at −90 °C. These well-resolved spectra could be nicely simulated by using the hyperfine coupling constants of nitrogens and protons on the phenyl group (see Table I). Radical cations $\mathbf{4}^{\bullet +}$ and $\mathbf{5}^{\bullet +}$ have clearly a "π-radical" structure, the spin density being delocalized on both diazo and phenyl groups.

The turnover of electronic structures by one-electron oxidation has been documented recently,[9] but the present case is the only clear-cut example. Relevant σ-radicals, e.g., iminoxyl,[10] benzoyl,[11]

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