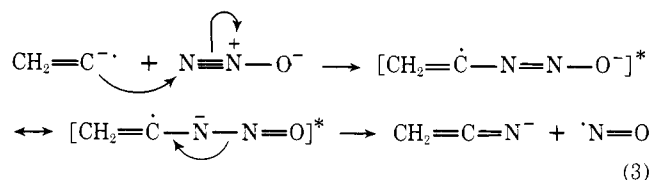


may readily be explained if one imagines that the stable C_2HF^- ions observed have the structure $CHF=C^-$, which can be derived with ease only from the 1,2 isomer. (In the absence of a sample of the trans compound we imagine that it will behave similarly to the cis isomer.) Thus there are now five pieces of evidence¹⁰ all pointing to the conclusion that stable $C_2H_2^-$ has the structure $CH_2=C^-$.

Smit and Field also discuss the reactions of a number of anions with neutral nitrous oxide which has the two main resonance structures $^-N=N^+=O$ and $N\equiv N^+ - O^-$.¹¹ Since the central atom in both resonance structures is positively charged, it is tempting to imagine (as do Smit and Field) that anionic attack will take place there. However, very detailed ¹⁵N and ¹⁸O labeling studies have been carried out on the O^-/N_2O system itself,¹² and in that case it was the considered opinion of the authors that the intermediate in the well-known reaction forming NO^- was of the form $(\cdot ON=NO^-)^*$. In previously unpublished work we have carried this matter a little further forward by studying again the related reaction of $CH_2=C^-$ with N_2O . Using specifically labeled ¹⁴N¹⁵N¹³O in standard ion cyclotron resonance drift cell experiments,¹⁴ we find that there is no incorporation of the ¹⁵N label into the CH_2CN^- product ions. Thus notwithstanding any initial electrostatic attraction to the central atom in nitrous oxide it seems that in the cases for which labeling results are available reaction actually takes place at the terminal nitrogen; in the case of $CH_2=C^-$ as shown in eq 3. The transitory gas-phase



reaction intermediate proposed in reaction 3 is expected to be favorable both because it is an unbranched odd-atom system and because of its analogy to the commonly observed conjugated alkoxide anions.¹⁵

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- The authors greatly acknowledge the cooperation of H. Dits in performing the MINDO/3 calculations.
- (i) The absence of any report of long-lived acetylene molecular anions; (ii) the discovery⁶ that $C_2H_2^-$ and $C_2D_2^-$, but not C_2HD^- , are the products of the reaction of O^- with $CH_2=CD_2$; (iii) the observation² of the reaction $C_2H_2^- + N_2O \rightarrow C_2H_2N^- + NO$; (iv) the calculations presented herein; (v) analogy with the difluoroethylene data presented here.
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J. H. J. Dawson, N. M. M. Nibbering*

Laboratory for Organic Chemistry, University of Amsterdam
Nieuwe Achtergracht 129, Amsterdam, The Netherlands

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Solid-State High Resolution NMR Spectroscopy of Spin $\frac{1}{2}$ Nuclei (¹³C, ²⁹Si, ¹¹⁹Sn) in Organic Compounds

Sir:

Proton-enhanced nuclear induction spectroscopy, which combines spin decoupling with polarization transfer in the rotating frame from the abundant protons to the isotopically rare or chemically dilute spins, provides a useful new technique for the study of the NMR spectra of solids.¹ In amorphous solids or microcrystalline powders, the presence of numerous anisotropy-broadened lines destroys the resolution achieved by dipolar decoupling, and high resolution can only be achieved by additional magic-angle sample spinning, which reduces the anisotropic chemical shifts to their isotropic averages.² This combination of techniques was first applied to polymers³ and shortly thereafter to powder samples.⁴

We have carried out preliminary experiments with some representative groups of organic compounds in order to establish the possibilities and limitations of this new technique. Several rather general conclusions about the solid-state ¹³C chemical shifts can be drawn from the data for some selected compounds,⁵ presented in Table I. (1) In the absence of specific solid-state effects, differences between the isotropic shift values measured in the neat liquid and a microcrystalline powder are small and do not exceed the usual solvent effects (see also Table II). (2) If the molecular structure has inversion symmetry in the liquid state, this is usually retained in the solid-state NMR spectrum. Other types of symmetry (such as reflection, etc.) are generally lost and additional line splittings appear. (3) The freezing of free rotation of bulky substituents leads to the formation of fixed conformations with the appearance of different chemical shifts for different geometrical arrangements of the interacting groups (see Table II). (4) Intramolecular nonbonded interactions predominate over the intermolecular ones. In *p*-dimethoxybenzene, the 1,4-nonbonded interactions between the substituent and the aromatic ring lead to unequal chemical shifts of the ortho carbons^{6,7} in a ξ -shaped conformation with the methyl groups located in the plane of the ring.⁸ (5) Intramolecular hydrogen bond formation leads to loss of molecular symmetry and to splitting of the spectral lines.⁹ (6) Large Knight shifts¹⁰ and the corresponding line splittings⁷ appear in the ¹³C spectra of charge-transfer complexes with one-dimensional metallic conductivity (-250 and -400 ppm in the tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ) complex).

As a general rule, in all solid silicon and tin compounds, where the proton T_1 is short enough for the ¹³C spectra to be obtained, the ²⁹Si and ¹¹⁹Sn NMR spectra can be measured as well. However, excessive complexation in the oxygenated and halogenated derivatives can lead to a very limited lattice mobility and very long proton T_1 values.

Table I. Comparison of ^{13}C Isotropic Shifts in the Solid and Liquid State

Compd	Sample	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	CH ₃
1,4-Dimethoxybenzene	<i>a</i>	153.8	112.5	118.6	153.8	112.5	118.6	54.5
	<i>b</i>	154.7	115.3	115.3	154.7	115.3	115.3	55.6
1,2,4,5-Tetramethoxybenzene	<i>a</i>	143.6	143.6	100.2	143.6	143.6	100.2	53.8; 56.7
	<i>b</i>	144.0	144.0	101.5	144.0	144.0	101.5	57.2
1,4-Diacetylbenzene	<i>a</i>	141.4	129.5	133.2	141.4	129.5	133.2	27.3
	<i>b</i>	141.1	128.3	128.3	141.4	128.3	128.3	26.1
1,4-Di- <i>tert</i> -butylbenzene	<i>a</i>	148.2	125.6	127.3	148.2	125.6	127.3	31.3 ^c
	<i>b</i>	148.2	125.2	125.2	148.2	125.2	125.2	32.0 ^c
Maleic acid	<i>a</i>	171.5	143.3	135.6	175.4			
	<i>d</i>	168.3	131.5	131.5	168.3			
Fumaric acid	<i>a</i>	172.7	138.3	138.3	172.7			
	<i>d</i>	167.3	134.5	134.5	167.3			

^a Powder sample at 20 °C. ^b Neat liquid just above the melting point. ^c Tertiary carbon ^{13}C shifts 34.1 ppm and 33.9 ppm, respectively. ^d 10% solution in ethanol.

Table II. ^{13}C , ^{29}Si , and ^{119}Sn Isotropic Shifts in Solid Organosilicon^a and Organotin Compounds

Compd	Si (M)	Si (Q)	$ \sigma_{\perp} - \sigma_{\parallel} _Q$	Sn	C, CH ₂	CH ₃
Q ₈ M ₈ ^{b,c}	12.6	-108.4	40			
Q ₈ M ₈ ^d	12.6	-108.4				
Q ₁₀ M ₁₀ ^{c,e}	11.7	-109.6				
Q ₁₀ M ₁₀ ^d	13.3	-109.3				
(NMe ₄) ₈ Si ₈ O ₂₀ ^{c,f}		-97.7 ^g	65			
K ₄ H ₄ Si ₄ O ₁₂ ^{c,h}		-89.2 ⁱ	78			
Ph ₃ SiOH ^c	-6.9 ^j					
(Me ₃ SiC ₆ H ₄) ₃ SiH ^c	-0.2 ^k		28			(0.5; -1.4) ^l
(<i>c</i> -C ₆ H ₁₁) ₄ Sn ^c				-92	29.5 ^m	
(<i>n</i> -C ₄ H ₉) ₂ SnCl ₂ ^c				280 ⁿ	30	15.8
(<i>n</i> -C ₄ H ₉) ₂ SnCl ₂ ^o				121.8	27 ^p	13.1

^a Q = Si(O_{1/2})₄; M = Si(CH₃)₃O_{1/2}. ^b Trimethylsilyl ester of octameric silicate with a double four-ring structure. ^c Powder sample at 20 °C. ^d 20% solution in benzene. ^e Trimethylsilyl ester of decameric silicate with a double five-ring structure. ^f Tetramethylammonium salt of octameric silicate with a double four-ring structure. ^g -98.6 ppm in 1.5 M water solution. ^h Potassium cyclotetrasilicate. ⁱ Rearranges in water solution. ^j -12.6 ppm in CHCl₃ solution; see E. A. Williams, J. D. Cargioli, and R. W. Larochele, *J. Organomet. Chem.*, **108**, 153 (1976). ^k $\sigma(\text{SiH}) = -9.4$ ppm. ^l Two lines with a 2:1 intensity ratio due to restricted rotation of the trimethylsilyl group. ^m One line due to close isotropic shifts. ⁿ Extremely broad line with a 200 ± 20 -ppm total width. ^o 68% solution in CHCl₃. ^p Three lines at 25.9, 26.6, and 26.9 ppm.

^{29}Si chemical shifts do not change appreciably upon crystallization. The possibility to study high resolution solid-state NMR spectra of both soluble and insoluble silicates and their trimethylsilyl esters¹¹ and tetraalkylammonium salts is most useful for the structural studies of these compounds, especially since many silicates with a well-defined molecular structure in the solid state tend to undergo very complicated rearrangement and condensation reactions in solution.¹²

A most unexpected solid state effect is the very large ^{119}Sn paramagnetic shift in solid di-*n*-butyltin dichloride. Increasing coordination and association with covalent bond formation usually leads to large ^{119}Sn diamagnetic shifts.¹³ A possible cause for this large paramagnetic shift would be ionization coupled with the formation of an irregular network of ion-bridged structures,¹⁴ which can lead to a large range of ^{119}Sn isotropic chemical shifts.¹⁵

The chemical-shift anisotropy values can also be easily measured by introducing slight deviations ($\pm 10^\circ$) from the magic angle of sample spinning;⁴ see Table II. In the case of ^{29}Si spectra, this provides additional information about deviations from tetrahedral symmetry in the SiO₄ groups and about the molecular geometry, such as the structure of siloxane rings.

The spectral resolution achieved, while not so good as in liquids, is adequate for most cases. All line widths were typically 10 ± 1 Hz, with the best value (8.5 Hz, equal to 0.6 ppm) achieved for ^{119}Sn in solid tetracyclohexyltin. A large-gap electromagnet ($H_0 = 9400$ G) and an air-driven turbine with 10-mm-o.d. glass rotors, rotated at speeds up to 4 kHz in a double-tuned crossed coil probe with adjustable angle between

\vec{H}_0 and $\vec{\omega}_r$,⁴ was used. A strong (up to 7 G) rf field was used for proton decoupling and the Hartmann-Hahn condition for efficient polarization transfer was fulfilled in all cases. The rf pulse sequences were generated by a modified NIC-293 input-output device, connected to a NIC-1085 computer, which was also used for signal accumulation and the fast Fourier transform. Pulse sequence repetition times were between 0.4 and 5 s (in some exceptional cases up to 100 s), depending upon the proton spin-lattice relaxation time T_1 . The proton T_1 values are reasonably short and solid-state high resolution spectra with a good signal to noise ratio can be obtained in compounds with some residual internal movement owing to the presence of rotating substituents, chain movement in polymers, or in the presence of paramagnetic species. The cross-polarization times ranged from 0.5 to 12 ms for all three nuclei. Right choice of the cross-polarization time is essential, because in some cases the proton $T_{1\rho}$ values can be very short and only use of the shortest possible cross-polarization time avoids losing some of the spectral lines.

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Endel T. Lippmaa,* Madis A. Alla, Tonis J. Pehk

Department of Physics, Institute of Cybernetics
of the Estonian Academy of Sciences
Tallinn 200001, U.S.S.R.

Günter Engelhardt

Central Institute of Physical Chemistry
of the Academy of Sciences of D.D.R.
Berlin, Adlershof, D.D.R.

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A Unique Two-Electron, Reversible Reduction of a Binuclear Copper(II) Complex. Observation of the Electrochemical Behavior Predicted by Polcyn and Shain for the Sequential Transfer of Two Electrons at the Same Potential

Sir:

Recently there have been reports of electrochemical investigations of systems in which two metal ions are chemically bound in close proximity.¹⁻³ Presumably, the object of this research is to study and develop systems which (a) exhibit novel multiple-electron redox processes and/or (b) mimic multiple-electron redox processes found in biological systems. Of particular interest in this regard are the enzymatic proteins containing type III coppers, e.g., laccase, tyrosinase, and hemocyanin. The type III copper centers are believed to contain two magnetically coupled Cu(II) ions⁴ which undergo a one-step, two-electron, reversible reduction to Cu(I), Cu(I).^{5,6} Such multielectron transfer reactions are apparently critical in the biological reductions of dioxygen. To our knowledge, all synthetic binuclear copper complexes that exhibit reversible reductions do so in (a) a one-electron reduction presumably yielding a Cu(I), Cu(II) product¹ or (b) two one-electron steps with a significant potential separation presumably yielding a Cu(I), Cu(I) product.⁷

This paper reports the first example of a synthetic system in which the molecule is reduced in two *sequential* reversible, one-electron steps having *identical* $E_{1/2}$ values. The net result of this process is the transfer of two electrons at the same potential.

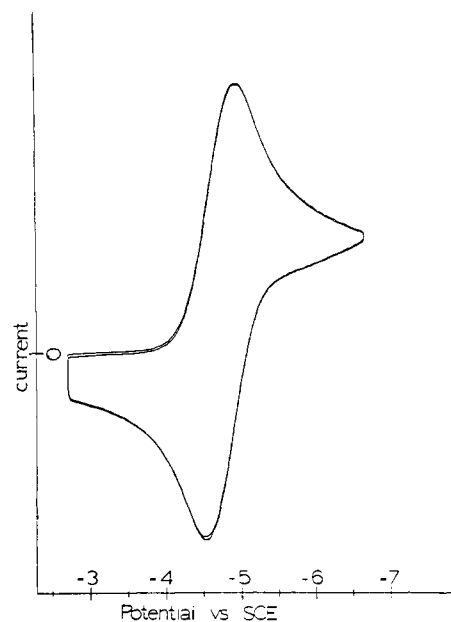
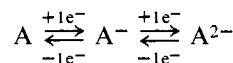
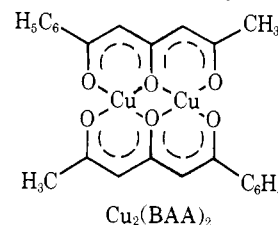


Figure 1. The cyclic voltammogram of $\text{Cu}_2(\text{BAA})_2$ in DMF, 0.1 M tetraethylammonium perchlorate at a hanging mercury drop electrode. Two scans are represented.



The molecule exhibiting the peculiar electrochemical properties described here is the neutral, binuclear copper(II) chelate of 1-phenyl-1,3,5-hexanetriconate(-2), $\text{Cu}_2(\text{BAA})_2$. A schematic drawing is shown. The synthesis, structure, and



magnetic properties of this compound have been previously reported.⁸ Structurally, the compound is best described as planar triketonate moieties with the two Cu(II) ions nearly in the plane and bridged by two ketonic oxygens forming a four-membered Cu_2O_2 ring. The two Cu(II) ions are strongly antiferromagnetically coupled with a singlet-triplet separation of 800 cm^{-1} . Thus, the compound is nearly diamagnetic at room temperature.

The cyclic voltammogram shown in Figure 1 is for the reduction of $\text{Cu}_2(\text{BAA})_2$ in DMF solution containing 0.1 M tetraethylammonium perchlorate at a hanging drop mercury electrode.⁹ Additional irreversible reductions are observed below -1.5 V. The reduction appears entirely reversible with a potential separation for the cathodic and anodic peaks of 42 mV. The peak separation is unaffected by changing the scan rates between 10 and 200 mV.s. The cathodic and anodic waves are of equal height regardless of the scan rate. A plot of the cathodic peak current vs. the square root of the scan rate yields a straight line ($r = 1.00$). The scan rate results are in agreement with the theoretical treatment of Nicholson and Shain¹⁰ for a reversible process. In addition, the waves are invariant as to whether the scan is begun from the anodic or cathodic side of the waves. All of these results are consistent with a reversible reduction but with a peak separation of 42 mV. The theory for multielectron transfer in stationary-electrode cyclic voltammetry has been developed by Polcyn and Shain.¹¹ For the case