7.14–7.50 (m, 9 H); ^{13}C NMR (CDCl$_3$) σ 31.6, 39.4, 123.8, 124.4, 125.3, 126.8, 126.9, 127.8, 128.5, 129.7, 139.1, 140.8, 144.3. (b) Several dihydro derivatives of *p*-terphenyl, such as as 1,4- and 5,6-dihydro-*p*-terphenyl, have been obtained by dissolved metal reductions of *p*-terphenyl. However, compound **3** (1,6-dihydro-*p*-terphenyl) cannot be prepared in this manner: Harvey, R. G.; Lindow, D. F.; Rabideau, P. W. *J. Am. Chem. Soc.* **1972,** *94,* 5412.

(9) *p*-Terphenyl: mp 208–210 °C (lit. mp 213 °C); the IR (KBr) and ^{1}H NMR spectra of our sample were identical with those reported for authentic *p*-terphenyl.

(10) Geske, D. H. *J. Phys. Chem.* **1959,** *63,* 1062.

(11) See, e.g. Kane-Maguire, L. A. P.; Mansfield, C. A. *J. Chem. Soc., Chem. Commun.* **1973,** 540.

(12) Only a small quantity of a mixture of 1,3-cyclohexadienetricarbonyliron and the dimer, 5,5′-bis(1,3-cyclohexadiene)hexacarbonyldiiron, was isolated.

(13) Similar migration of an aryl group has been observed in the oxidation of tetraarylborate ions.[3] (For a detailed discussion of this and related rearrangements, see Eisch, J. J. *Adv. Organomet. Chem.* **1977,** *16,* 67.) The intramolecular nature of the migration has been demonstrated in the cases of electrochemical and ceric ion oxidation[3c] and appears to obtain with other oxidants as well.[3e]

(14) Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Verlag Chemie-Academic Press: Germany, 1970.

(15) (a) Similar mechanistic arguments for ortho attack have been offered in the reaction of CH$_3$OSO$_2$F and the tri-*n*-butyl-1-naphthylborate ion (Negishi and Merrill, ref 2a). (b) Facile oxidation of the dihydro derivative obtained from deboronation of the *E* isomer under the reaction conditions (degassed solvents; inert atmosphere) or nonconcerted loss of the elements of Ph$_2$BH from the *E* isomer of **4** would appear unfavorable.

(16) The initial electron transfer and subsequent phenyl migration in mechanism Bb parallels that suggested for the oxidation of Ph$_4$B$^-$ by metallic species, as well as by DDQ.[3e]

(17) Burton, R.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961,** 594. Dauben, H. J., Jr.; Bertelli, D. J. *J. Am. Chem. Soc.* **1961,** *83,* 497.

(18) An attempt to oxidatively deboronate the possible intermediate **4** by treatment of the reaction products obtained in THF with $^-$OH/H$_2$O$_2$ failed to yield complex **2** or any evidence for the free ligand **3.** In CH$_3$CN (with or without H$_2$O) the only characterizable complexes were 1,3-cyclohexadienetricarbonyliron and the dimer 5,5′-bis(cyclohexadiene)hexacarbonyldiiron.

(19) Perrin, C. L.; Skinner, G. A. *J. Am. Chem. Soc.* **1971,** *93,* 3389.

(20) Unpublished observations, this laboratory.

B. R. Reddy, J. S. McKennis*
Department of Chemistry, Oklahoma State University
Stillwater, Oklahoma 74074

Received August 13, 1979

Transfer of CIDNP via Proton Exchange and Nuclear Overhauser Effect

Sir:

It is typically assumed that, if a molecule displays CIDNP,[1] its polarized nuclei experience a hyperfine coupling in an intermediate paramagnetic state. We point out here that CIDNP can become transferred *intermolecularly,*[2] for example,[3] via chemical exchange[4] of spin polarized protons. Furthermore, the well-known nuclear Overhauser effect (NOE)[5] causes a secondary nuclear spin polarization in all those nuclei which are coupled by either scalar ("negative NOE") or dipolar ("positive NOE") interactions to the exchanging protons. Consequently, "*inert*" molecules may display "CIDNP" deceptively, whereas this phenomenon is really a "chemically induced (or 'pumped') NOE" (CINOE). The latter may complicate the analysis of CIDNP spectra, but it may also be exploited for the following applications: (a) selective signal enhancement of protons and of other nuclei (^{15}N), (b) assignment assistance for specific resonances (for example α protons in alcohols), and (c) study of proton exchange and the dynamics thereof.

The concept of CINOE follows readily from the polarization transfer experiments of Hoffman and Forsén[6] together with the known negative or positive NOE associated with chemical exchange of spin polarized protons.[5] Whereas NOE is typically "pumped" electronically, CINOE offers certain advantages: (a) the initial polarization can be orders of magnitude larger (by the enhancement factor of CIDNP[1]) than those generated electronically; (b) the sign of the transferred polarization can conveniently be chosen to be either positive or negative by changing one of the parameters connected by Kaptein's rules of CIDNP[7] or the recent additions thereto;[8] (c) broad resonances can be pumped too. The latter allows pumping of the broad resonances of protons attached to ^{14}N (or any other fast relaxing quadrupole nucleus), since only the T_2 and not the T_1 of these protons is short.[5] Electronically such broad resonances are very difficult if not impossible to pump. Figure 1 illustrates the results for formamide (2×10^{-3} mol/L) and Figure 1b for the ^{15}N enriched (95%) species. In addition to the NMR spectra[9] the CINOE spectra are shown (Figure 1a′ and 1b′), obtained by using equimolar mixtures (8×10^{-3} mol/L) of biphenyl-d_{10} and triethylamine (TEA) in CD$_3$CN as solvent for a pump. The spectra were recorded on a slightly modified Varian HA 100 spectrometer in an all-quartz probe during UV irradiation with the NiSO$_4$-filtered[10] light of a 1 kW mercury–xenon lamp (Hanovia 977B-1).

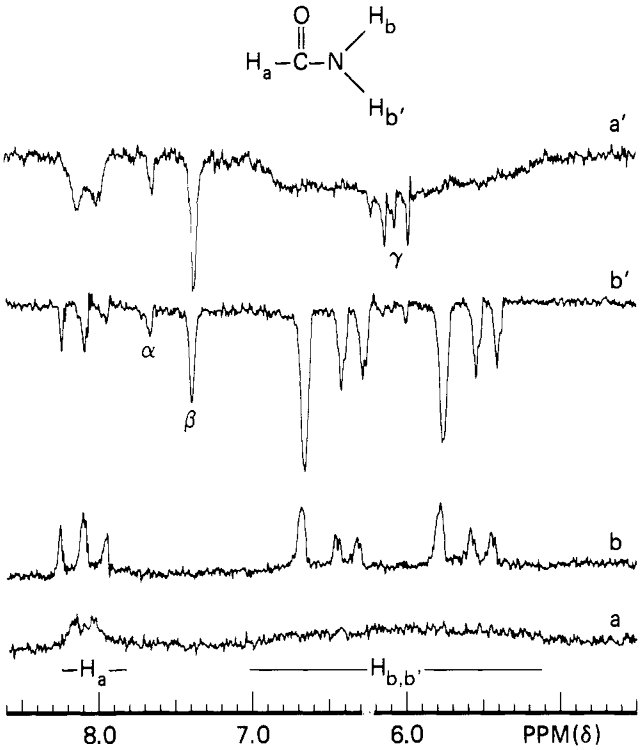


Figure 1. NMR spectra of formamide (a) and of formamide-^{15}N (b) in CD$_3$CN and CINOE spectra (a′ and b′).

A prerequisite for CINOE studies, namely an efficient pump was found in photoinduced electron-transfer reactions between tertiary aliphatic amines as donors and a variety of acceptors (A) listed in Table I. The α protons namely, i.e., the protons attached to the α carbons of the tertiary amine derived radical

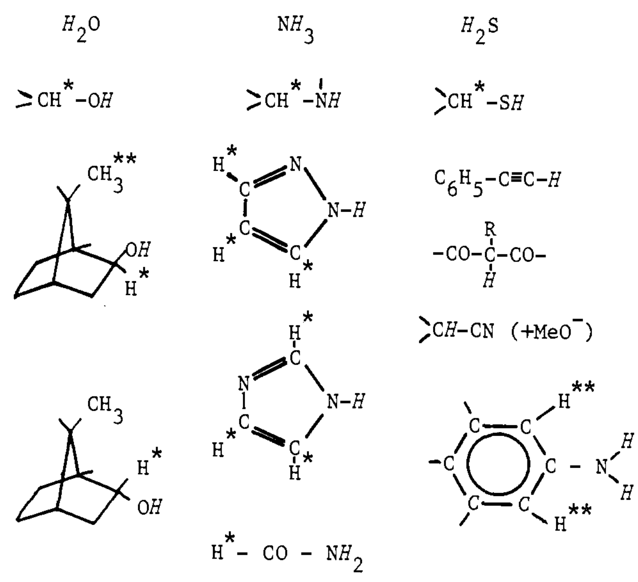
Table I

acceptor	donor	polarized in -*H*	-H*	-H**
biphenyl	TEA	E	E	A
naphthalene	TEA	E	E	A
naphthalene	CH$_3$CH$_2$CH$_2$N(CH$_3$)$_2$	E	E	A
naphthalene	CH$_3$CH$_2$CD$_2$N(CD$_3$)$_2$		none	
naphthalene	*N*-alkylpyrrole	A	A	E
CD$_3$CN	TEA	A	A	E
C$_6$H$_5$CN	TEA	A	A	E
benzophenone	TEA	A	A	E
anthraquinone	TEA	A	A	E

[a] E denotes emission, A absorption. For explanation of -*H*, -H*, and -H**, cf. Chart I.

0002-7863/79/1501-7732$01.00/0

Chart I[a]

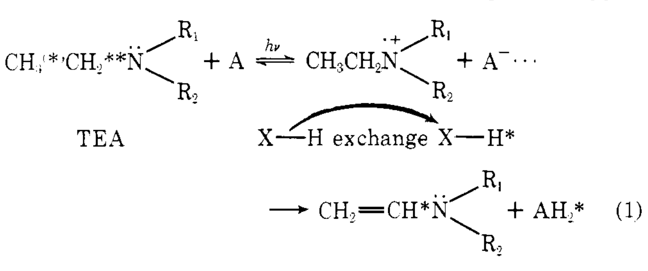


[a] H* = negative NOE (scalar coupling); H** = positive NOE (dipolar coupling); *H* = exchanging protons.

cations are *acidic* and exchange readily with the marked protons (-*H*) in the functional groups listed in Chart I.

Many reactions which generate aminium cations and their associated CIDNP have been outlined previously.[2,8a,11] These photoinduced electron-transfer reactions require polar solvents ($\epsilon > 20$) such as acetonitrile or dimethyl sulfoxide. The acceptors may be (a) aliphatic or aromatic nitriles,[11a] (b) aromatic hydrocarbons,[11b] or (c) ketones or quinones.[11c] Table I lists the sign (phase) of CIDNP observed in the α protons of the amines (-H**) and of the exchanging protons (-*H*), which is always opposite. Chart I correlates the CINOE observed in characteristic substrates.

The chemistry of the pump as well as the associated NMR and CIDNP lines should be compatible with the substrate. Some overlap of resonances is acceptable, such as resonance γ in Figure 1a′, which stems from the oxidation product diethylvinylamine (DEVA) derived from TEA (vide infra). The peaks α and β in Figure 1 are due to the ortho and para positions of biphenyl whose protons exchange with those of the aminium and of the substrates. The pump should also be highly reversible to assure a long duration of the CINOE. Nitriles and hydrocarbons were found to yield a higher reversibility than quinones or ketones. The irreversibility could be shown to be due to photoreduction of A to the dihydro form AH_2 and simultaneous oxidation (and possibly hydrolysis) of the amine to an eneamine, such as DEVA from TEA (eq 1). In support



$$CH_3{}^{(*)}CH_2{}^{**}\ddot{N}R_1R_2 + A \underset{}{\overset{h\nu}{\rightleftharpoons}} CH_3CH_2\overset{\cdot +}{N}R_1R_2 + A^{-}\cdots$$

$$X-H \text{ exchange } X-H^*$$

$$\longrightarrow CH_2{=}CH^*\ddot{N}R_1R_2 + AH_2{}^* \quad (1)$$

TEA

DEVA

of the above scheme the CIDNP resonances of the eneamines and of AH_2 are observed. Furthermore, the polarization in the positions -*H*, -H*, and H** disappears upon deuteration of the α positions in the amines; cf. the difference between $CH_3CH_2CH_2N(CH_3)_2$ and $CH_3CH_2CD_2N(CD_3)_2$ in Table I. In presence of suitable bases (methoxide) even the solvent CD_2HCN displays CINOE because of the equilibrium $CH_3O^- + CD_3CN \rightleftharpoons CH_3OD + CD_2CN^-$ and subsequent exchange. Water can become strongly polarized, especially when occurring in small concentrations in aprotic solvents. This fact may be used to pump aqueous systems via a membrane together with a flow system.

The molecules investigated here (Chart I) are models for those of biochemical interest, such as sugars, nucleic acids, etc. There CINOE might well be quite selective. Especially attractive seems the possibility of pumping ^{15}N, where electronic pumps are inefficient because of the negative magnetic moment of ^{15}N and the associated negative enhancement, which causes an initial signal loss. CINOE could provide a superior alternative for positive ^{15}N signal enhancement. The above proton results seem encouraging.

References and Notes

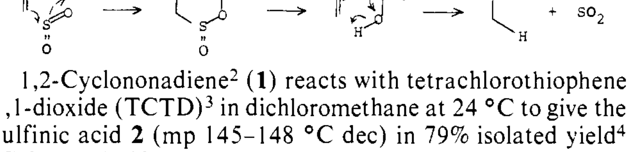
(1) *NATO Adv. Study Inst. Chem. Induced Magn. Polar., Ser. C34, 1977,* **1977**, and references therein.
(2) Intramolecular CINOE has been reported by: (a) Closs, G. L.; Czeropski, M. S. *Chem. Phys. Lett.* **1977**, *45*, 115; **1978**, *53*, 321. (b) Kaptein, R.; Dijkstra, K.; Müller, F.; van Schlagen, G. J. *J. Magn. Reson.* **1978**, *31*, 171.
(3) Complexation or hydrogen bonding provide other alternatives. We found intermolecular transfer of CINOE from TEA$^+$ to a crown-6 ether due to hydrogen bonding.
(4) Johnson, C. S. *Adv. Magn. Reson.* **1965**, *1*, 33, and references therein.
(5) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.
(6) Forsén, R.; Hoffman, R. A. *J. Chem. Phys.* **1963**, *39*, 2829; **1964**, *40*, 1189; *Acta Chem. Scand.* **1963**, *17*, 1787.
(7) Kaptein, R. *J. Am. Chem. Soc.* **1972**, *94*, 6251.
(8) (a) Bargon, J., ref 1, Chapter XXIII. (b) Closs, G. L.; Czeropski, M. S. *J. Am. Chem. Soc.* **1977**, *99*, 6172. (c) Bargon, J. *J. Am. Chem. Soc.* **1977**, *99*, 8350.
(9) For complete analysis of the NMR spectra see: Sunners, B.; Piette, L. H.; Schneider, W. G. *Can. J. Chem.* **1960**, *38*, 681.
(10) Kasha M. *Opt. Soc. Am.* **1948**, *38*, 929.
(11) (a) Bargon, J. *Proc. Congr. AMPERE, 19th, 1976* **1976**, 145. (b) Roth, H. D. *Mol. Photochem.* **1973**, *5*, 91. (c) Roth, H. D.; Manion, M. L. *J. Am. Chem. Soc.* **1975**, *97*, 6886.
(12) IBM Visiting Scientist from the Instituto Policattedra de Chimica Organica, University of Parma, 43100 Parma, Italy.

Joachim Bargon,* G. P. Gardini[12]
IBM Research Laboratory
San Jose, California 95193
Received August 29, 1979

Annelation of 1,2-Cyclononadiene with Tetrachlorothiophene Dioxide. An Ene Reaction with Sulfur Dioxide

Sir:

Rogić and Masilamani[1] have proposed that the isomerization of olefins with sulfur dioxide involves an ene reaction to form an allylic sulfinic acid which undergoes 1,3 rearrangement, followed by a retro-ene reaction to give the isomerized olefin and sulfur dioxide. Direct evidence for the presence of the sulfinic acid is lacking. We report the isolation of a stable sulfinic acid in an ene reaction of an olefin with sulfur dioxide.



1,2-Cyclononadiene[2] (**1**) reacts with tetrachlorothiophene 1,1-dioxide (TCTD)[3] in dichloromethane at 24 °C to give the sulfinic acid **2** (mp 145–148 °C dec) in 79% isolated yield[4] (Scheme I). If the reaction is run in refluxing carbon tetrachloride, sulfur dioxide escapes from the reaction mixture and the triene **3** (mp 51–52 °C) and **2**, which is stable under these conditions, are isolated in 52 and 9% yields, respectively. When sulfur dioxide is passed into a solution of **3** in dichloromethane, an ene reaction occurs and the sulfinic acid **2** precipitates (76%

0002-7863/79/1501-7733$01.00/0