

time-dependent perturbation theory<sup>3</sup> it follows that the evolution of the singlet character from the initial zero-order triplet spin state will be proportional to  $(H_{ST}/\Delta E)^2$ , where  $H_{ST}$  is the nuclear spin dependent matrix element of the hyperfine Hamiltonian and  $\Delta E$  is the difference between the energy of the zero-order singlet and triplet states. When intersystem crossing caused by this mechanism is in competition with that caused by spin-orbit coupling, it is apparent that the most intense CIDNP spectra will be those in which the biradical is created in a magnetic field such that  $g\beta H_0 = 2J$ , implying a maximum in the intensity vs. field curve at the point where the Zeeman energy equals the singlet-triplet splitting.

A real biradical of type II is constantly changing its conformation, giving a distribution of singlet-triplet splittings over its lifetime. Thus, a field-dependence plot should show a maximum at that field for which  $g\beta H_0 = \langle 2J \rangle_{av}$ , where  $\langle 2J \rangle$  is the weighted average of the singlet-triplet splitting over all conformations. Table I lists these averages for the biradicals of type II included in this study.

Table I

Ketone	Curve max, cm <sup>-1</sup>	Width at half-height, cm <sup>-1</sup>
IV	>1.31 <sup>a</sup>	>2.0 <sup>b</sup>
Ia	1.87 ± 0.28	~2.3 <sup>b</sup> ± 0.5
Ib	0.374 ± 0.037	0.527 ± 0.03
Ic	0.196 ± 0.009	0.257 ± 0.02
Id	0.0854 ± 0.003	0.0448 ± 0.003
Ie	0.0261 ± 0.005	0.0304 ± 0.005

<sup>a</sup> Due to limitation of experimentally available magnitude of  $H_0$  the maximum could not be determined. <sup>b</sup> Estimated, assuming a symmetrical curve.

The fact that  $J$  decreases as the length of the biradical increases is consistent with three exchange mechanisms: (1) indirect exchange through the  $\sigma$  bonds, (2) exchange *via* the solvent molecules, (3) direct exchange through space.<sup>7</sup> Some evidence on the exchange mechanism can be obtained by comparison of our work with that of Glarum and Marshall, who used esr to study the carbonate diester of 2,2,6,6-tetramethyl-4-piperidonyl-1-oxyl. This stable, relatively rigid biradical has localized radical centers separated by 15 Å and ten  $\sigma$  bonds. In chloroform solution at 40°,  $2J = 0.0028$  cm<sup>-1</sup> (30 G).<sup>8</sup> In IIe, the radical centers are separated by 13 Å in the fully extended conformation and are also ten  $\sigma$  bonds apart, yet  $J$  is an order of magnitude larger. This discrepancy cannot be explained by mechanism 1 for IIe. Mechanism 1 is probably also unimportant for IIa-d, since these biradicals should spend very little time in the fully extended conformation.

(3) Perturbation theory is used here for brevity. The well known<sup>4-6</sup> full solution requires the solution of the time-dependent Schrödinger equation for all states, but the qualitative results are the same.

(4) G. L. Closs and A. D. Trifunac, *J. Amer. Chem. Soc.*, **92**, 2183 (1970).

(5) J. I. Morris, R. C. Morrison, D. W. Smith, and J. F. Garst, *ibid.*, **94**, 2406 (1972).

(6) R. Kaptein and J. A. de Hollander, *ibid.*, **94**, 6269 (1972).

(7) C. Herring in "Magnetism," Vol. IIB, G. T. Rado and H. Suhl, Ed., Academic Press, New York, N. Y., 1966, pp 1-181.

(8) S. H. Glarum and J. H. Marshall, *J. Chem. Phys.*, **47**, 1374 (1967); cf. R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rasset, and P. Rey, *Bull. Soc. Chim. Fr.*, 3290 (1965).

The full interpretation of the variation in width of the field-dependence curves must include a consideration of the random fluctuations in  $J$  due to changes in conformation, the relative densities of states for the transitions involved, the relative contributions of hyperfine and spin-orbit coupling, and the lifetime of the states. This last consideration, *i.e.*, lifetime broadening, provides by itself at least a qualitative understanding. If the reasonable assumption is made that the singlet state of the biradical has a very short lifetime inversely related to the length of the biradical ( $10^{-10}$ - $10^{-12}$  sec), then the uncertainty broadening of the singlet energy qualitatively reproduces the observed variation in width. A more quantitative interpretation will rest on a consideration of all the effects involved and is in progress.

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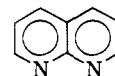
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### A Binuclear Complex of 1.5 Valent Nickel

Sir:

In the last years the coordinating properties of 1,8-naphthyridine (napy) have been intensively studied.<sup>1</sup>



We have found that from the reaction of anhydrous nickel(II) halides (1 mmol) with napy (2 mmol) and sodium tetraphenylborate (1 mmol) in 1-butanol (60 ml) a pale green compound (I) with the general formula  $[\text{Ni}(\text{napy})_2\text{X}]\text{B}(\text{C}_6\text{H}_5)_4$  (X = halogen) is formed. This product is insoluble in common organic solvents. The magnetic moments are 3.34 and 3.36 BM for the chloro- and bromo complexes, respectively, clearly corresponding to nickel(II) compounds.

If the reaction solution is heated to boiling without separating the initial green product, the solution slowly darkens and eventually shining black crystals begin to separate from the greenish black solution. Recrystallization of the black product (II) from acetone effects separation from any remaining green product (I). Product II has the formula  $[\text{Ni}_2(\text{napy})_4\text{X}_2]\text{B}(\text{C}_6\text{H}_5)_4$  (X = halogen, NCS,  $\text{NO}_3$ ) and contains therefore nickel in the formal oxidation state 1.5. Analogous complexes  $[\text{Ni}_2(\text{napy})_4\text{X}_2]\text{PF}_6$  (III) are formed when  $\text{NaPF}_6 + \text{NaBH}_4$  is used in ethanol instead of  $\text{NaB}(\text{C}_6\text{H}_5)_4$ . In this case the greenish black color appears immediately and no green intermediate product is observed.

The magnetic moments per nickel atom in both II and III vary from 2.91 to 3.07 BM, but are in the range 4.19-4.34 BM for the dimeric complexes. These values are consistent with the presence of three unpaired electrons in the dimer. The dependence of  $1/\chi$  on temperature is linear in the range 88-293°K for the bromo derivative with a  $\theta$  value of  $-3^\circ\text{K}$ .

(1) D. G. Hendricker, *Inorg. Chem.*, **8**, 2328 (1969); T. E. Reed and D. G. Hendricker, *Inorg. Chim. Acta*, **4**, 471 (1970); D. G. Hendricker and R. L. Bodner, *Inorg. Chem.*, **9**, 273 (1970); R. L. Bodner and D. G. Hendricker, *ibid.*, **12**, 33 (1973); D. G. Hendricker and R. J. Foster, *ibid.*, **12**, 349 (1973).

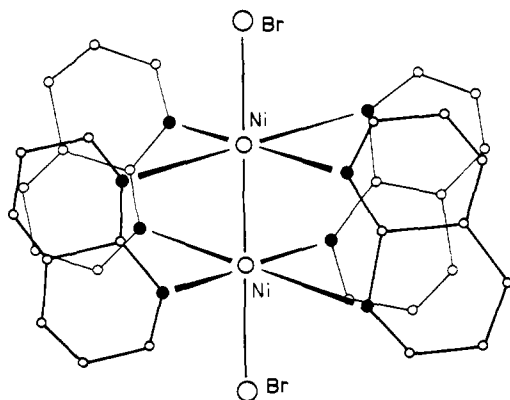


Figure 1. Sketch of the  $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$  dimeric cations: ○, carbon atoms; ●, nitrogen atoms.

All the II and III complexes behave as 1:1 electrolytes in nitroethane. The electronic spectra, which are identical for both the tetraphenylborate and hexafluorophosphate series, are practically unchanged on passing from the solid to solution in nitroethane, suggesting that the structure of the solid is retained in solution. The spectra are characterized by a very intense absorption above 14 kK with two maxima, one in the 24–25-kK range ( $\epsilon_m \approx 3500\text{--}4000$  for the dimers) and the other in the 15.5–17.5-kK range ( $\epsilon_m \approx 2500$ ). A third far less intense band occurs in the 9–10-kK region ( $\epsilon_m \approx 100$ ). On changing the anion X, all the maxima are shifted in accordance with the spectrochemical series.

A single-crystal X-ray study of the bromo derivative of the tetraphenylborate series has shown that this compound contains discrete  $[\text{Ni}_2(\text{napy})_4\text{Br}_2]^+$  cations and  $\text{B}(\text{C}_6\text{H}_5)_4^-$  anions.

Crystals of dibromotetrakis(1,8-naphthyridine)dinickel tetraphenylborate ( $\text{C}_{56}\text{H}_{44}\text{N}_8\text{Br}_2\text{BNi}_2$ ) are shiny black monoclinic prisms:  $a = 9.931(3)$ ,  $b = 32.311(8)$ ,  $c = 16.535(9)$  Å;  $\beta = 101.5(3)^\circ$ ;  $U = 5191.04$  Å<sup>3</sup>; mol wt = 1116.38;  $D_{\text{measd}} = 1.41$  (by flotation),  $Z = 4$ ,  $D_{\text{calcd}} = 1.43$ ; space group  $P2_1/c$  (from systematic absences).

Intensity data were measured by a Philips computer-controlled single-crystal diffractometer PW 1100, using Mo K $\alpha$  radiation monochromatized with a flat graphite monochromator crystal.

The structure was solved by Patterson and Fourier methods, using 2403 independent observed reflections ( $I > 3\sigma$ ). The refinement of the coordinates and the thermal parameters was carried out by the method of least squares. At the present the  $R$  factor is 8.8% using anisotropic thermal model for all of the nickel, bromine, and nitrogen atoms in the cell. Refinement is continuing.

In the complex cation all four molecules of napy are bridge bonded, each through its two nitrogens, to two nickel atoms which are 2.421(5) Å apart (Figure 1). Each metal atom is coordinated in a square-planar array by four nitrogen atoms (of four ligand molecules) which are coplanar within 0.010(11) Å. The two superimposed planes are parallel within  $0.2^\circ$ . The average Ni–N distance in the plane is 2.10(2) Å.

The coordination polyhedron is completed by two bromine atoms which lie in apical position, one for

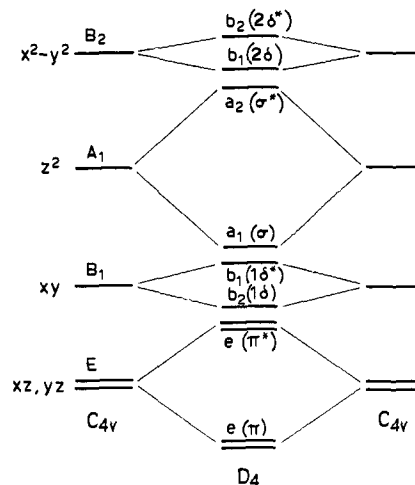


Figure 2. Molecular orbital energy scheme for the  $\text{Ni}_2(\text{napy})_4\text{X}_2$  dimers. The orbitals are labeled according to the assumed  $D_4$  symmetry and to the  $C_{\infty v}$  perturbation due to the Ni–Ni interaction.

each nickel atom. The average Ni–Br distance is 2.635(5) Å and the average Br–Ni–N<sub>basal</sub> angle is 93.6(0.6)°.

The chromophore can thus be described as being made up of two equivalent moieties in which each nickel atom is coordinated by five donor atoms arranged in a square pyramid, four nitrogen atoms forming the base and one bromine atom the apex. Each nickel atom is on the average 0.135 Å above the basal plane.

The symmetry of this complex can be considered as roughly  $D_4$ ; *i.e.*, the two  $\text{NiN}_4\text{Br}$  halves are practically half way between the eclipsed and the staggered conformation. The whole coordination polyhedron can be described as a bicapped tetragonal prism twisted toward a bicapped tetragonal antiprism, the “twist angle” being  $25^\circ$ .

The nickel–nickel distance of 2.42 Å is short compared with the corresponding distance in metallic nickel, 2.49 Å,<sup>2</sup> suggesting that some metal–metal interaction is operative in our compound. Nickel–nickel distances in the range 2.38–2.56 Å had been previously reported for a few nickel(II) complexes with bridged stereochemistry.<sup>3,4</sup> Although the electronic spectra cannot be easily interpreted in the absence of more detailed studies, a qualitative MO picture analogous to the one previously proposed for the dimeric copper acetate hydrate<sup>5</sup> can be used to rationalize the observed magnetic moments which correspond to three unpaired electrons. The energies of the two  $\text{NiN}_4\text{Br}$  chromophores can be evaluated through a ligand field approach; the metal–metal interaction produces a splitting of these levels, and 17 valence electrons are to be accommodated in ten molecular orbitals (Figure 2). As in the case of copper acetate we suggest that the three highest energy levels are quite close to each other so that a quadruplet ground level can be expected.

**Acknowledgment.** Thanks are due to Mr. G. Scapacci

- (2) L. E. Sutton, *Chem. Soc. Spec. Publ.*, No. 18 (1965).
- (3) M. Corbett and B. F. Hoskins, *Chem. Commun.*, 1602 (1968).
- (4) M. Bonamico, G. Dessy, and V. Fares, *Chem. Commun.*, 697, 1106 (1969).
- (5) L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, 16, 1385 (1962).

for technical assistance in the preparation of the compounds.

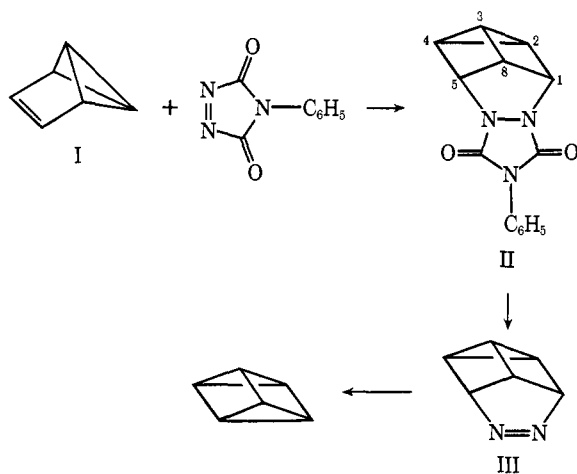
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 Received January 18, 1973

## Synthesis of Prismane

Sir:

Although derivatives have been prepared,<sup>1</sup> the simple molecule C<sub>6</sub>H<sub>6</sub> known as prismane,<sup>2</sup> in which six carbon-hydrogen units are disposed at the corners of a triangular prism, has never been synthesized and only rarely theorized upon<sup>3</sup> since Ladenburg first proposed its structure for benzene 104 years ago.<sup>4</sup> We have now prepared pure samples of prismane by the procedure indicated in Scheme I. The last step of the synthesis is

Scheme I



an adaptation of a method tried by Trost and Cory in a previous attempt to prepare prismane<sup>5,6</sup> and has been used to make other hydrocarbons.<sup>7-14</sup> The steps

(1) (a) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964); (b) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); (c) R. Criegee and R. Askani, *Angew. Chem., Int. Ed. Engl.*, **5**, 519 (1966); (d) D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, **88**, 5934 (1966); (e) W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem., Int. Ed. Engl.*, **6**, 78 (1967); (f) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc. C*, 1232 (1970); (g) D. M. Lemal, J. V. Staros, and V. Austel, *J. Amer. Chem. Soc.*, **91**, 3373 (1969); (h) M. G. Barlow, J. G. Dingwall, and R. N. Haszeldine, *Chem. Commun.*, 1580 (1970).

(2) Tetracyclo[2.2.0.0<sup>2,6</sup>.0<sup>3,5</sup>]hexane.

(3) (a) M. Randić and Z. Majerski, *J. Chem. Soc. B*, 1289 (1968); (b) Y. Tejiro, K. Simizu, and H. Kato, *Bull. Chem. Soc. Jap.*, **41**, 2336 (1968); (c) N. C. Baird and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **91**, 352 (1969); (d) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) A. Ladenburg, *Chem. Ber.*, **2**, 140 (1869).

(5) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5573 (1971).

(6) Both pyrolysis and photolysis were tried.

(7) The cleavage of nitrogen from an azo compound was first used to prepare a strained hydrocarbon by Criegee and Rimmelin.<sup>8</sup> The use of light to effect the reaction was introduced subsequently.<sup>9</sup>

(8) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

(9) (a) T. V. Van Auken and K. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **84**, 3736 (1962); (b) K. Kocsis, P. G. Ferrini, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **43**, 2178 (1960); (c) C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

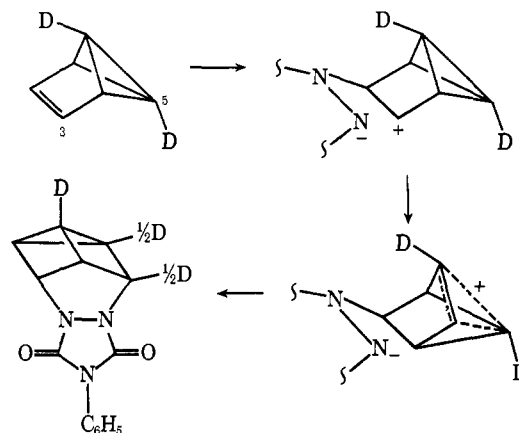
(10) (a) E. L. Allred and J. C. Hinshaw, *J. Amer. Chem. Soc.*, **90**, 6885 (1968); (b) H. Tanida, S. Teratake, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5341, 5345 (1969); (c) L. A. Paquette and L. M. Leichter, *J. Amer. Chem. Soc.*, **92**, 1765 (1970).

leading to the azo precursor III<sup>15</sup> are unorthodox.

Combining benzvalene (I)<sup>18</sup> in ether-dioxane with the powerful dienophile<sup>19</sup> 4-phenyltriazolinedione<sup>13,20</sup> (ice cooled, then set at room temperature for 1 hr) gives, after passage through silica gel using CHCl<sub>3</sub> eluent, in 50-60% yield, a 1:1 adduct, mp 173-175°, of structure II.<sup>21</sup> Refluxing with KOH in CH<sub>3</sub>OH-H<sub>2</sub>O (85:15, v/v) for 24 hr, extraction, and treatment with acidic CuCl<sub>2</sub> then yields a cuprous chloride derivative, which with aqueous NaOH<sup>22</sup> gives azo compound III (65% yield after crystallization from pentane and sublimation).<sup>16,23</sup>

The mechanism by which II forms is revealed by 5,6-dideuterated benzvalene<sup>24</sup> with 4-phenyltriazolinedione giving adduct labeled as indicated in Scheme II.<sup>26</sup> The

Scheme II



favored path therefore is analogous to that followed by bromine in adding to benzvalene<sup>24,27</sup> and once thought to be followed by azodicarboxylic esters in adding to

(11) The method was once reported to have given quadricyclane,<sup>12</sup> but the experiment could not be repeated.<sup>13</sup> Attempts to use it to make cubane failed.<sup>14</sup>

(12) R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).

(13) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(14) J. P. Snyder and D. G. Farnum, quoted in D. W. McNeil, M. E. Kent, E. Hedaya, P. F. D'Angelo, and P. O. Schissel, *J. Amer. Chem. Soc.*, **93**, 3817 (1971).

(15) The previous synthesis<sup>16</sup> follows a path similar to one leading to prostaglandins.<sup>17</sup>

(16) B. M. Trost and R. M. Cory, *J. Amer. Chem. Soc.*, **93**, 5572 (1971).

(17) E. J. Corey, N. M. Weinshenker, T. K. Schaaf, and W. Huber, *J. Amer. Chem. Soc.*, **91**, 5675 (1969).

(18) T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971). The average yield now is 45%.

(19) J. Sauer and B. Schröder, *Chem. Ber.*, **100**, 678 (1967).

(20) R. C. Cookson, S. S. Gupte, I. D. R. Stevens, and C. T. Watts, *Org. Syn.*, **51**, 121 (1971).

(21) Mass spectrum: *m/e* 253 (parent, 4%), 119 (base peak, C<sub>6</sub>H<sub>5</sub>-NCO). Pmr (CDCl<sub>3</sub>):  $\tau$  2.55 (m, 5.00 H, phenyl), 4.98 (d of t, *J* = 4.5, 1.3 Hz, 1.93 H, H<sub>1,5</sub>), 6.86 (quintet of d, *J* = 4.5, 0.95, 1.02 Hz, H<sub>3</sub>), 7.37 (t of d, *J* = 3.4, 0.95 Hz, 1.03 H, H<sub>2</sub>), 7.66 (m, 2.02 H, H<sub>2,4</sub>); cf. similar spectrum in ref 16.

(22) O. Diels, J. H. Blom, and W. Koll, *Justus Liebigs Ann. Chem.*, **443**, 242 (1925).

(23) Explosive.

(24) R. J. Roth, Dissertation, Columbia University, 1972. The deuteration was achieved by combining benzvalene in ether with *n*-butyllithium and then adding D<sub>2</sub>O.<sup>25</sup> 92% of the 5,6 hydrogens were replaced by deuteriums.

(25) (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **85**, 2022 (1963); (b) J. Meinwald, C. Swithenbank, and A. Lewis, *ibid.*, **85**, 1880 (1963); (c) E. Galantay, N. Paolella, S. Barcza, R. V. Coombs, and H. P. Weber, *ibid.*, **92**, 5771 (1970).

(26) The ratio of the intensities of the resonances at  $\tau$  2.55, 4.98, 6.86, 7.37, and 7.66 is 5.04:1.48:0.99:<0.05:1.48. The resonance at 6.82 is now a quartet with no fine splitting and that at 7.66 is a doublet of doublets.

(27) R. J. Roth and T. J. Katz, *J. Amer. Chem. Soc.*, **94**, 4770 (1972).