

In the studies with added nitrate and acetone, both of these electron scavengers<sup>11</sup> reduced the H<sub>2</sub>S yields to low values when present at high concentrations. With added acetone the limiting value of  $G(\text{H}_2\text{S})$  is about 0.3, roughly half of the "residual" H atom yield.<sup>12</sup> This yield might be expected from a partitioning of the "residual" hydrogen atoms between reactions 3 and 5.



Added nitrate reduced the H<sub>2</sub>S yield to nearly zero as would be expected if the nitrate acted as has been postulated<sup>13</sup> as both an efficient electron and hydrogen atom scavenger. From the linear plots obtained in each of these competition studies, ratios of rate constants were calculated and are reported here.

$$k_4(e_{\text{aq}}^- + \text{RSH})/k_2(e_{\text{aq}}^- + \text{NO}_3^-) = 0.4$$

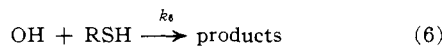
$$k_4(e_{\text{aq}}^- + \text{RSH})/k_1(e_{\text{aq}}^- + \text{CH}_3\text{COCH}_3) = 0.9$$

From these ratios another ratio may be calculated, namely

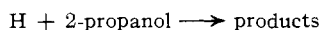
$$k_2(e_{\text{aq}}^- + \text{NO}_3^-)/k_1(e_{\text{aq}}^- + \text{CH}_3\text{COCH}_3) = 2.2$$

This value may be favorably compared with 1.9 calculated from the data of Hart and co-workers<sup>11</sup> obtained with the pulsed-electron technique.

Similar competition kinetic studies with *p*-nitrosodimethylaniline, a compound whose chromophoric group has been shown<sup>14</sup> to be attacked specifically by OH radicals, show the rate constant for reaction 6 to be



about  $3 \times 10^9$  l. mole<sup>-1</sup> sec.<sup>-1</sup>, a nearly diffusion-controlled reaction rate constant. A preliminary study in which 2-propanol was used as an H atom competitor was complicated by the additional OH competition but showed that the total rate constant for reactions 3 and 5 is at least on the same order of magnitude as that for



It is apparent from the above experiments that cysteine, one of the better protective agents, is a quite effective OH and hydrated-electron scavenger. Preliminary studies in our laboratory indicate similar behavior for several other two- and three-carbon atom protective amino thiols.<sup>15</sup> These studies are being expanded to include other thiols which have shown no biological protective action.

Convincing experimental evidence has been presented for mechanisms of protection other than "radical scavenging."<sup>2-4</sup> However, in view of the results reported above which support diffusion-controlled or nearly diffusion-controlled scavenging of the two major reactive intermediates known to exist in neutral, irradiated aqueous solutions, we wish to suggest that it is only reasonable to include the possibility that many of these reactive intermediates are scavenged *before* they are able to attack sensitive biological molecules. By combining the results of our studies with those reported by Hart, *et al.*,<sup>11</sup> it is observed that oxygen has a rate constant for combination with hydrated electrons which is approximately four times as large as cysteine.

(13) J. Rabani, *J. Phys. Chem.*, **67**, 1609 (1963).

(14) I. Kraljic and C. Trumbore, paper presented at the 147th National Meeting of the American Chemical Society, Denver, Colo., Jan., 1964.

(15) Generously provided through Dr. David Jacobus of the Walter Reed Army Research Institute.

These results may help to explain the enhanced biological protective effect of *anoxia* in the presence of cysteine.<sup>2</sup>

More detailed studies on cysteine and related sulfhydryl compounds are in progress and will be reported elsewhere.<sup>16</sup>

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(16) A. El Samahy, H. L. White, and C. N. Trumbore, submitted for publication.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF DELAWARE  
NEWARK, DELAWARE

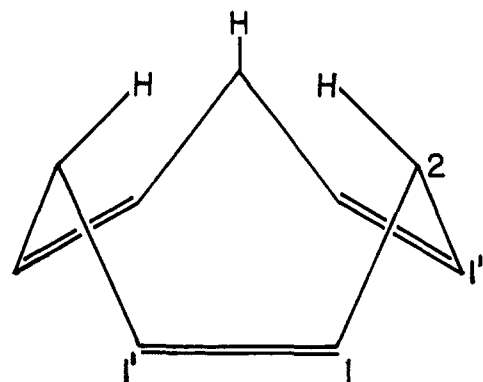
A. EL SAMAHY  
H. L. WHITE  
C. N. TRUMBORE

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### On the Question of Homoconjugation in *cis,cis,cis*-1,4,7-Cyclononatriene<sup>1</sup>

Sir:

*cis,cis,cis*-1,4,7-Cyclononatriene has recently been obtained independently in three different laboratories.<sup>2-4</sup> Proton magnetic resonance studies indicate that the substance possesses an interconverting crown-to-crown structure (I) in the liquid phase. On the basis of



I

simple LCAO-MO calculations, Radlick and Winstein<sup>2</sup> have predicted a "nonzero" delocalization energy, resulting from "trishomo"<sup>5</sup> conjugation, for this triene. A more quantitative treatment by Untch<sup>3</sup> suggests that such delocalization energy is negligible. We wish to report experimental results which, within the limits of their uncertainties, exclude the possibility that homoallylic stabilization makes any significant contribution to the ground state of the cyclononatriene molecule.

The heat of hydrogenation of *cis,cis,cis*-1,4,7-cyclononatriene measured in acetic acid solution at 25° is  $-76.88 \pm 0.05$  kcal./mole. The value obtained for *cis*-cyclononene is  $-23.62 \pm 0.07$  kcal./mole.<sup>6</sup> The heat evolved in the hydrogenation of triolefin to monoolefin is therefore 53.3 kcal./mole, which represents an average value of  $-26.7$  kcal./mole for the heat of

(1) This research was supported by grants from the National Science Foundation and the Robert A. Welch Foundation.

(2) P. Radlick and S. Winstein, *J. Am. Chem. Soc.*, **85**, 344 (1963).

(3) K. G. Untch, *ibid.*, **85**, 345 (1963); K. G. Untch and R. J. Kurland, *ibid.*, **85**, 346 (1963).

(4) W. R. Roth, *Ann.*, **671**, 10 (1964).

(5) Cf. S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3244 (1961).

(6) R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957).

hydrogenation of the first two double bonds of cyclo-natriene. The latter figure, if anything, seems a little high in view of the well recognized nonbonded repulsion phenomenon associated with medium-sized rings and in comparison with the standard reference value of  $-27.1$  kcal./mole for cyclohexene.<sup>7</sup> It is possible that cyclo-natriene possesses some degree of strain, since it is estimated that the three intraannular methylene hydrogens (*cf.* I) lie slightly within the conventional (intermolecular) van der Waal's distance for nonbonded hydrogen atoms (see below). The hydrogenation results can be interpreted as indicating (a) the absence of ground state homoconjugative stabilization in cyclo-natriene, or (b) essential equivalence of stabilizing and destabilizing forces in this molecule. A compelling argument in favor of the former view is provided by X-ray crystallographic measurements.

Small needle-like crystals of *cis,cis,cis*-1,4,7-cyclo-natriene were selected for X-ray diffraction investigation. Rotation and Weissenberg photographs showed the crystals to be hexagonal with unit cell constants  $a = 11.977$  Å. and  $c = 4.65$  Å. at  $T = -35^\circ$ . The only observed systematic condition limiting possible reflections was  $-h + k + l = 3n$ . Observed density measurements agree with calculated values assuming three molecules per unit cell. Of the various possible space groups,  $C_{3v}^5-R3m$  was chosen on the basis of expected molecular symmetry and packing. Subsequent refinement showed this choice to be the correct one. A trial structure was postulated assuming a crown structure for the molecule with carbon atom 1 in the general positions  $18c$  and carbon atom 2 in the special positions  $9b$ .<sup>8</sup>

Intensity data were collected at  $-35^\circ$  using  $l = 0, 1,$  and  $2$  layer Weissenberg photographs. The individual layers were correlated using zero layer precession data from the  $a$  axis. Intensities were visually estimated and reduced to a set of  $|F|$ 's in the usual manner. A total of 86 independent reflections was observed and subsequently was used in a full matrix isotropic least-squares treatment on the trial structure. The final parameters obtained from this refinement are

$$\begin{array}{llll} x_1 = 0.1746 & y_1 = 0.0311 & z_1 = 0 & B_1 = 7.3 \\ x_2 = 0.0856 & & z_2 = 0.1820 & B_2 = 8.1 \end{array}$$

The final value for the reliability index  $R$  is 12%. No attempt was made to include the hydrogen atoms in the refinement.

The refined molecular structure has the point symmetry  $C_{3v}$  required by the crystal space group. The observed interatomic distances and angles are given in Table I. The bonded distances are normal for a non-conjugated unsaturated cyclic hydrocarbon. The  $C_1-C_2-C_1''$  angle of  $108^\circ$  and the nonbonded  $C \dots C_1''$  distance of 2.46 Å. preclude the possibility of any meaningful homoaromaticity in the molecule.

TABLE I

$C_1-C_2$	1.52 Å.	$C_1'-C_1-C_2$	$124^\circ$
$C_1=C_1'$	1.34 Å.	$C_1-C_2-C_1''$	$108^\circ$
$C_1 \dots C_1''$	2.46 Å.		

The  $C_1'-C_1-C_2$  angle of  $124^\circ$  is slightly larger than normal. The deviation of this angle from  $120^\circ$  has

(7) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(8) "International Tables for X-ray Crystallography," Vol. I, Kynoch Press, Birmingham, Eng., 1952.

the effect of separating the nonbonded intraannular methylene hydrogen atoms. If one assumes that the methylene  $C_2-H$  distance is 1.09 Å. and the  $C_1-C_2-H$  bond angle is tetrahedral, then the intraannular nonbonded  $H \dots H$  approach distance is calculated to be 1.95 Å. This distance is about 0.2 Å. longer than the value calculated on the basis of a  $C_1'-C_1-C_2$  angle of  $120^\circ$  and about 0.2 Å. shorter than the accepted van der Waal's distance of 2.2 Å. The observed X-ray crystal structure and the heat of hydrogenation are consistent with the suggestion of a small amount of strain in the molecule.

INSTITUTE FOR ORGANIC CHEMISTRY  
UNIVERSITY OF COLOGNE  
COLOGNE, GERMANY

W. R. ROTH

DEPARTMENT OF CHEMISTRY  
RICE UNIVERSITY  
HOUSTON, TEXAS

W. B. BANG  
P. GOEBEL  
R. L. SASS  
R. B. TURNER  
A. P. YÜ

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## A Novel Chemiluminescent Electron-Transfer Reaction

Sir:

We have discovered a new type of chemiluminescent reaction which promises to be one of the most general types known. It involves the abstraction of an electron from an aromatic hydrocarbon radical anion by a suitable oxidizing agent.

Reactions in solution which liberate a large amount of energy within a time short compared to that required for diffusion out of a solvent cage are of particular interest because of the possibility of reaching an excited electronic level in one of the products. The transfer of an electron from an aromatic hydrocarbon radical anion to the corresponding radical cation ( $R^{\cdot-} + R^{\cdot+} \rightarrow 2R$ ) is of this type and has the advantage that it may be coupled to a reasonably efficient fluorescent system.

A chemiluminescent reaction between electro-generated anthracene positive and negative radical ions has been observed by Hoijtink and co-workers.<sup>1</sup> More recently, evidence was presented<sup>2</sup> for this type of reaction in  $\gamma$ -irradiated naphthalene in a rigid matrix. Upon gradual thawing of the matrix, both the fluorescence and the phosphorescence of naphthalene were observed. These observations are related to the recombination luminescence originally discovered in Lewis' laboratory.<sup>3,4</sup> This process, involving the discharge of a photo-ionized molecule in a rigid matrix by an electron, can yield singlet and/or triplet excited states.<sup>4-6</sup> Here the interaction of the electron with the acceptor is of paramount importance.

We had originally intended to study the reactions between the ions ( $R^{\cdot+}$  and  $R^{\cdot-}$ ,  $R^{+2}$  and  $R^{-2}$ ) derived from 9,10-diphenylanthracene (DPA). DPA was chosen because it has a good fluorescence efficiency and because it appeared to be a particularly stable species

(1) Professor Hoijtink (Amsterdam) mentioned these results during a visit in the summer of 1963.

(2) B. Brocklehurst, G. Porter, and J. M. Yates, *J. Phys. Chem.*, **68**, 203 (1964).

(3) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944), and references therein.

(4) H. Linschitz, M. G. Berry, and D. Schweitzer, *ibid.*, **76**, 5833 (1954).

(5) E. C. Lim and G. W. Swenson, *J. Chem. Phys.*, **36**, 118 (1962).

(6) E. C. Dolan and A. C. Albrecht, *ibid.*, **37**, 1149 (1962); **38**, 567 (1963).