

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.⁷ 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 $9b$.⁸

Intensity data were collected at -35° 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° 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°
$C_1=C_1'$	1.34 Å.	$C_1-C_2-C_1''$	108°
$C_1 \dots C_1''$	2.46 Å.		

The $C_1'-C_1-C_2$ angle of 124° is slightly larger than normal. The deviation of this angle from 120° 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° 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.¹ More recently, evidence was presented² for this type of reaction in γ -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.^{3,4} 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.⁴⁻⁶ 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).

whose most reactive centers are sterically blocked, attributes which should favor simple electron transfer rather than bond formation. A deep blue solution of K^+DPA^- was easily prepared by treating a slight excess of DPA with potassium in boiling THF.^{7,8} Unfortunately, our attempts to prepare DPA^+ and DPA^{+2} were fruitless.⁹

We then used the 9,10-dichloride of DPA ($DPACl_2$) as a potential source of DPA^{+2} . Indeed, it reacted instantly with K^+DPA^- giving a bright chemiluminescence which was visually identified as the fluorescence of DPA. The luminescent reaction is probably not a simple bimolecular process but is possibly termolecular: $DPACl_2 + 2DPA^- \rightarrow 2DPA + DPA^* + 2Cl^-$. The K^+DPA^- may be aggregated at this concentration (0.04 M) in THF. We also found chemiluminescence during the reaction of sodium naphthalene with $DPACl_2$ (THF solution). The general framework of recombination luminescence is still capable of providing an explanation at this point. Phosphorescent emission, commonly associated with this process, would not occur in fluid solution. Fluorescence might, however, result from triplet-triplet annihilation.¹⁰

Further investigation of the reactions of K^+DPA^- with various electron acceptors has shown that chemiluminescence in these systems is a more general phenomenon than had been heretofore supposed. The rapid luminescent reaction of K^+DPA^- with Cl_2 may be rationalized by assuming the intermediate formation of $DPACl_2$. However, bright chemiluminescence also accompanies the reaction of K^+DPA^- with benzoyl peroxide, oxalyl chloride, mercuric chloride, and aluminum chloride, cases in which the intermediacy of reducible, oxidized DPA derivatives is quite unlikely. We measured the emission spectrum of the benzoyl peroxide reaction and found it to be the same as the fluorescence spectrum of DPA (both in dioxane). The sole nonacidic product of this reaction is DPA.¹¹ Thus it appears that the reaction of a good oxidizing agent (where neither it nor its reduction product is a quencher) with DPA^- is capable of producing singlet excited DPA. The available data do not implicate the triplet. The chemiluminescent process is not limited to hydrocarbon ions and we expect that radical anions derived from various fluorescent species will exhibit this behavior. For example, the green solution (ether) obtained from the reaction of sodium with N-methylacridone, undoubtedly containing the ketyl, affords a bright chemiluminescence (visually the same as N-methylacridone fluorescence) upon reaction with benzoyl peroxide.

The luminescent reaction of DPA^- with reagents such as benzoyl peroxide cannot be explained easily within the established framework of recombination luminescence. We postulate that the luminescent reaction

(7) Cf. R. Gerdil and E. A. C. Lucken, *Helv. Chim. Acta*, **44**, 1966 (1961).

(8) Tetrahydrofuran was distilled from the sodium ketyl of benzophenone. All reactions were run under nitrogen.

(9) We abandoned these experiments upon learning from Professor Harold Hart of Michigan State University that his experiments had indicated that internal cyclization occurred readily in cations derived from DPA. We are grateful to him for informing us of his results and for permission to quote them prior to publication.

(10) C. A. Parker and C. G. Hatchard, *Proc. Chem. Soc.*, 147 (1962); *Proc. Roy. Soc. (London)*, **269**, 570 (1962).

(11) The reaction was carried out in ether. After evaporation of the solvent (N_2), the residue was treated with NaOH-EtOH (3 hr., 25°). The infrared spectrum of the nonacidic, crystalline product was identical with that of DPA.

involves *only the transfer of an electron from DPA^- to the acceptor*. One possible explanation for the chemiluminescence is that this reaction (which could proceed by electron tunneling) liberates energy within a small volume in a time which is very short compared to that required for its escape as heat to the medium at large. This energy may be accepted by a molecule within the solvent cage which has an accessible electronic state. The question of the relative nuclear geometries of R, R^- , and R^* and the importance of any differences in bond lengths may be raised at this point. Clearly, if $R^- \rightarrow R + e^-$ is to be followed quickly by $R \rightarrow R^*$, the geometry of R must be such that it can readily accept the energy. We do not feel that much can be said at this point other than to note that both R^- and R^* would be expected to have longer bond lengths than R and that they may be closer in geometry to each other than they are to R. An alternative model may be based on simple orbital theory. In this picture the effective result of the electron-transfer process is that the electron which is transferred is one from the highest bonding level of the radical ion R^- , and thus directly generates an excited state of R.

We wish to point out our disagreement with a view that has appeared frequently in the literature. A reaction is *not* likely to generate a product in an excited electronic state merely because it provides sufficient energy to do so. In a reaction which involves bond formation and/or cleavage, the energy is not likely to be liberated as fast as it is in a reaction involving only the transfer of an electron. Instead, the energy is likely to be liberated relatively slowly and absorbed as bond vibrations in several molecules as the transition state is traversed.

We intend to investigate other reactions involving electron transfer and we hope to extend the generality of our observations.

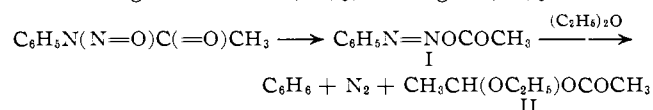
BELL TELEPHONE LABORATORIES, INC. EDWIN A. CHANDROSS
MURRAY HILL, NEW JERSEY FRIEDRICH I. SONNTAG
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Decomposition Reactions of N-Nitrosoacetanilide¹

Sir:

It is well established that N-nitrosoacetanilide rearranges to phenyldiazo acetate (I). The mechanisms by which I reacts have been the subject of considerable investigation and controversy.² It is the purpose of this report to describe experiments which have a bearing on this issue.

Decomposition of I in diethyl ether proceeds smoothly at 25° to give benzene (52%), nitrogen (59%), and 1-



ethoxyethyl acetate (II, 22%).³ In another experiment, treatment of the reaction mixture with 2,4-dinitrophenylhydrazine afforded a 50% yield of acetal-

(1) Research supported in part by the U. S. Army Research Office, Durham, N. C.

(2) (a) H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, pp. 153-159; (b) E. L. Eliel, M. Eberhardt, O. Simamura, and S. Meyerson, *Tetrahedron Letters*, **No. 17**, 749 (1962); (c) D. H. Hey and M. J. Perkins, *ibid.*, **No. 7**, 445 (1963).

(3) The benzene yields were determined by ultraviolet analysis. The structure assignment of II rests on infrared and n.m.r. analysis and its formation of acetaldehyde 2,4-dinitrophenylhydrazine.